

10/586490

=> file registry
FILE 'REGISTRY' ENTERED AT 15:32:42 ON 01 FEB 2008
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STRUCTURE FILE UPDATES: 31 JAN 2008 HIGHEST RN 1001228-41-6
DICTIONARY FILE UPDATES: 31 JAN 2008 HIGHEST RN 1001228-41-6

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TSCA INFORMATION NOW CURRENT THROUGH June 29, 2007

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=> file caplus
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FILE COVERS 1907 - 1 Feb 2008 VOL 148 ISS 6
FILE LAST UPDATED: 31 Jan 2008 (20080131/ED)

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'OBI' IS DEFAULT SEARCH FIELD FOR 'CPLUS' FILE

=> d stat que L40
L2 1 SEA FILE=REGISTRY ABB=ON PLU=ON 4635-87-4
L4 1 SEA FILE=REGISTRY ABB=ON PLU=ON 74-90-8
L5 1 SEA FILE=REGISTRY ABB=ON PLU=ON 106-99-0
L9 2 SEA FILE=REGISTRY ABB=ON PLU=ON "3-PENTENENITRILE, ("?/CN
L10 3 SEA FILE=REGISTRY ABB=ON PLU=ON L2 OR L9
L11 2 SEA FILE=REGISTRY ABB=ON PLU=ON (16529-66-1/CRN OR 16545-78-1

/CRN OR 4635-87-4/CRN)

| | | | |
|---------|--------------------------------|--------|---|
| L13 | 5 SEA FILE=REGISTRY ABB=ON | PLU=ON | L10 OR L11 |
| L17 | 1 SEA FILE=REGISTRY ABB=ON | PLU=ON | "3-PENTENENITRILE-2,2-D2"/CN |
| L18 | 6 SEA FILE=REGISTRY ABB=ON | PLU=ON | L13 OR L17 |
| L21 | 17208 SEA FILE=CAPLUS ABB=ON | PLU=ON | L4 |
| L22 | 24982 SEA FILE=CAPLUS ABB=ON | PLU=ON | L5 |
| L25 | 130 SEA FILE=CAPLUS ABB=ON | PLU=ON | L18 (L) PREP/RL |
| L26 | 3070185 SEA FILE=CAPLUS ABB=ON | PLU=ON | (RACT OR RCT OR RGT)/RL |
| L27 | 2588 SEA FILE=CAPLUS ABB=ON | PLU=ON | L21 (L) L26 |
| L28 | 9152 SEA FILE=CAPLUS ABB=ON | PLU=ON | L22 (L) L26 |
| L29 | 32 SEA FILE=CAPLUS ABB=ON | PLU=ON | L27 AND L28 AND L25 |
| L30 | 297092 SEA FILE=CAPLUS ABB=ON | PLU=ON | ?POROUS/?BI |
| L31 | 40403 SEA FILE=CAPLUS ABB=ON | PLU=ON | MICROPOR/?BI |
| L32 | 30953 SEA FILE=CAPLUS ABB=ON | PLU=ON | MOLECULAR SIEV/?BI |
| L33 | 128603 SEA FILE=CAPLUS ABB=ON | PLU=ON | ZEOLIT/?BI |
| L34 | 23369 SEA FILE=CAPLUS ABB=ON | PLU=ON | MESOPOR/?BI |
| L35 | 1378 SEA FILE=CAPLUS ABB=ON | PLU=ON | ADSORBANT/?BI |
| L36 | 375297 SEA FILE=CAPLUS ABB=ON | PLU=ON | CERAMIC/?BI |
| L40 | 1 SEA FILE=CAPLUS ABB=ON | PLU=ON | L29 AND (L30 OR L31 OR L32 OR L33 OR L34 OR L35 OR L36) |

=> d stat que L41

| | | | |
|---------|--------------------------------|--------|--|
| L2 | 1 SEA FILE=REGISTRY ABB=ON | PLU=ON | 4635-87-4 |
| L4 | 1 SEA FILE=REGISTRY ABB=ON | PLU=ON | 74-90-8 |
| L5 | 1 SEA FILE=REGISTRY ABB=ON | PLU=ON | 106-99-0 |
| L9 | 2 SEA FILE=REGISTRY ABB=ON | PLU=ON | "3-PENTENENITRILE, (?/CN |
| L10 | 3 SEA FILE=REGISTRY ABB=ON | PLU=ON | L2 OR L9 |
| L11 | 2 SEA FILE=REGISTRY ABB=ON | PLU=ON | (16529-66-1/CRN OR 16545-78-1 /CRN OR 4635-87-4/CRN) |
| L13 | 5 SEA FILE=REGISTRY ABB=ON | PLU=ON | L10 OR L11 |
| L17 | 1 SEA FILE=REGISTRY ABB=ON | PLU=ON | "3-PENTENENITRILE-2,2-D2"/CN |
| L18 | 6 SEA FILE=REGISTRY ABB=ON | PLU=ON | L13 OR L17 |
| L21 | 17208 SEA FILE=CAPLUS ABB=ON | PLU=ON | L4 |
| L22 | 24982 SEA FILE=CAPLUS ABB=ON | PLU=ON | L5 |
| L25 | 130 SEA FILE=CAPLUS ABB=ON | PLU=ON | L18 (L) PREP/RL |
| L26 | 3070185 SEA FILE=CAPLUS ABB=ON | PLU=ON | (RACT OR RCT OR RGT)/RL |
| L27 | 2588 SEA FILE=CAPLUS ABB=ON | PLU=ON | L21 (L) L26 |
| L28 | 9152 SEA FILE=CAPLUS ABB=ON | PLU=ON | L22 (L) L26 |
| L29 | 32 SEA FILE=CAPLUS ABB=ON | PLU=ON | L27 AND L28 AND L25 |
| L37 | 54059 SEA FILE=CAPLUS ABB=ON | PLU=ON | AIR/CT |
| L38 | 18350 SEA FILE=CAPLUS ABB=ON | PLU=ON | NOBLE GAS/?BI |
| L39 | 15276 SEA FILE=CAPLUS ABB=ON | PLU=ON | HELIOUM GROUP/?BI |
| L41 | 1 SEA FILE=CAPLUS ABB=ON | PLU=ON | L29 AND (L37 OR L38 OR L39) |

=> d stat que L42

| | | | |
|---------|----------------------------|--------|--|
| L2 | 1 SEA FILE=REGISTRY ABB=ON | PLU=ON | 4635-87-4 |
| L4 | 1 SEA FILE=REGISTRY ABB=ON | PLU=ON | 74-90-8 |
| L5 | 1 SEA FILE=REGISTRY ABB=ON | PLU=ON | 106-99-0 |
| L9 | 2 SEA FILE=REGISTRY ABB=ON | PLU=ON | "3-PENTENENITRILE, (?/CN |
| L10 | 3 SEA FILE=REGISTRY ABB=ON | PLU=ON | L2 OR L9 |
| L11 | 2 SEA FILE=REGISTRY ABB=ON | PLU=ON | (16529-66-1/CRN OR 16545-78-1 /CRN OR 4635-87-4/CRN) |
| L13 | 5 SEA FILE=REGISTRY ABB=ON | PLU=ON | L10 OR L11 |
| L17 | 1 SEA FILE=REGISTRY ABB=ON | PLU=ON | "3-PENTENENITRILE-2,2-D2"/CN |
| L18 | 6 SEA FILE=REGISTRY ABB=ON | PLU=ON | L13 OR L17 |

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| | | | | |
|-----|--------|------------------------|--------|---|
| L21 | 17208 | SEA FILE=CAPLUS ABB=ON | PLU=ON | L4 |
| L22 | 24982 | SEA FILE=CAPLUS ABB=ON | PLU=ON | L5 |
| L23 | 383 | SEA FILE=CAPLUS ABB=ON | PLU=ON | L18 |
| L24 | 47 | SEA FILE=CAPLUS ABB=ON | PLU=ON | L21 AND L22 AND L23 |
| L30 | 297092 | SEA FILE=CAPLUS ABB=ON | PLU=ON | ?POROUS?/BI |
| L31 | 40403 | SEA FILE=CAPLUS ABB=ON | PLU=ON | MICROPOR?/BI |
| L32 | 30953 | SEA FILE=CAPLUS ABB=ON | PLU=ON | MOLECULAR SIEV?/BI |
| L33 | 128603 | SEA FILE=CAPLUS ABB=ON | PLU=ON | ZEOLIT?/BI |
| L34 | 23369 | SEA FILE=CAPLUS ABB=ON | PLU=ON | MESOPOR?/BI |
| L35 | 1378 | SEA FILE=CAPLUS ABB=ON | PLU=ON | ADSORBANT?/BI |
| L36 | 375297 | SEA FILE=CAPLUS ABB=ON | PLU=ON | CERAMIC?/BI |
| L37 | 54059 | SEA FILE=CAPLUS ABB=ON | PLU=ON | AIR/CT |
| L38 | 18350 | SEA FILE=CAPLUS ABB=ON | PLU=ON | NOBLE GAS?/BI |
| L39 | 15276 | SEA FILE=CAPLUS ABB=ON | PLU=ON | HELUM GROUP?/BI |
| L42 | 2 | SEA FILE=CAPLUS ABB=ON | PLU=ON | L24 AND (L30 OR L31 OR L32 OR L33 OR L34 OR L35 OR L36 OR L37 OR L38 OR L39) |

=> d stat que L61

| | | | | |
|-----|-------|--------------------------|--------|---|
| L2 | 1 | SEA FILE=REGISTRY ABB=ON | PLU=ON | 4635-87-4 |
| L4 | 1 | SEA FILE=REGISTRY ABB=ON | PLU=ON | 74-90-8 |
| L5 | 1 | SEA FILE=REGISTRY ABB=ON | PLU=ON | 106-99-0 |
| L9 | 2 | SEA FILE=REGISTRY ABB=ON | PLU=ON | "3-PENTENENITRILE, (/?/CN |
| L10 | 3 | SEA FILE=REGISTRY ABB=ON | PLU=ON | L2 OR L9 |
| L11 | 2 | SEA FILE=REGISTRY ABB=ON | PLU=ON | (16529-66-1/CRN OR 16545-78-1 /CRN OR 4635-87-4/CRN) |
| L13 | 5 | SEA FILE=REGISTRY ABB=ON | PLU=ON | L10 OR L11 |
| L17 | 1 | SEA FILE=REGISTRY ABB=ON | PLU=ON | "3-PENTENENITRILE-2,2-D2"/CN |
| L18 | 6 | SEA FILE=REGISTRY ABB=ON | PLU=ON | L13 OR L17 |
| L21 | 17208 | SEA FILE=CAPLUS ABB=ON | PLU=ON | L4 |
| L22 | 24982 | SEA FILE=CAPLUS ABB=ON | PLU=ON | L5 |
| L23 | 383 | SEA FILE=CAPLUS ABB=ON | PLU=ON | L18 |
| L24 | 47 | SEA FILE=CAPLUS ABB=ON | PLU=ON | L21 AND L22 AND L23 |
| L60 | 1 | SEA FILE=REGISTRY ABB=ON | PLU=ON | 1344-28-1 |
| L61 | 4 | SEA FILE=CAPLUS ABB=ON | PLU=ON | L60 AND L24 |

=> d stat que L63

| | | | | |
|-----|--------|--------------------------|--------|---|
| L2 | 1 | SEA FILE=REGISTRY ABB=ON | PLU=ON | 4635-87-4 |
| L4 | 1 | SEA FILE=REGISTRY ABB=ON | PLU=ON | 74-90-8 |
| L5 | 1 | SEA FILE=REGISTRY ABB=ON | PLU=ON | 106-99-0 |
| L9 | 2 | SEA FILE=REGISTRY ABB=ON | PLU=ON | "3-PENTENENITRILE, (/?/CN |
| L10 | 3 | SEA FILE=REGISTRY ABB=ON | PLU=ON | L2 OR L9 |
| L11 | 2 | SEA FILE=REGISTRY ABB=ON | PLU=ON | (16529-66-1/CRN OR 16545-78-1 /CRN OR 4635-87-4/CRN) |
| L13 | 5 | SEA FILE=REGISTRY ABB=ON | PLU=ON | L10 OR L11 |
| L17 | 1 | SEA FILE=REGISTRY ABB=ON | PLU=ON | "3-PENTENENITRILE-2,2-D2"/CN |
| L18 | 6 | SEA FILE=REGISTRY ABB=ON | PLU=ON | L13 OR L17 |
| L21 | 17208 | SEA FILE=CAPLUS ABB=ON | PLU=ON | L4 |
| L22 | 24982 | SEA FILE=CAPLUS ABB=ON | PLU=ON | L5 |
| L23 | 383 | SEA FILE=CAPLUS ABB=ON | PLU=ON | L18 |
| L24 | 47 | SEA FILE=CAPLUS ABB=ON | PLU=ON | L21 AND L22 AND L23 |
| L62 | 314410 | SEA FILE=CAPLUS ABB=ON | PLU=ON | ALUMINA/BI |
| L63 | 4 | SEA FILE=CAPLUS ABB=ON | PLU=ON | L24 AND L62 |

=> d stat que L66

| | | | | |
|----|---|--------------------------|--------|-----------|
| L2 | 1 | SEA FILE=REGISTRY ABB=ON | PLU=ON | 4635-87-4 |
|----|---|--------------------------|--------|-----------|

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L4 1 SEA FILE=REGISTRY ABB=ON PLU=ON 74-90-8
L5 1 SEA FILE=REGISTRY ABB=ON PLU=ON 106-99-0
L9 2 SEA FILE=REGISTRY ABB=ON PLU=ON "3-PENTENENITRILE, ("?/CN
L10 3 SEA FILE=REGISTRY ABB=ON PLU=ON L2 OR L9
L11 2 SEA FILE=REGISTRY ABB=ON PLU=ON (16529-66-1/CRN OR 16545-78-1
/CRN OR 4635-87-4/CRN)
L13 5 SEA FILE=REGISTRY ABB=ON PLU=ON L10 OR L11
L17 1 SEA FILE=REGISTRY ABB=ON PLU=ON "3-PENTENENITRILE-2,2-D2"/CN

L18 6 SEA FILE=REGISTRY ABB=ON PLU=ON L13 OR L17
L21 17208 SEA FILE=CAPLUS ABB=ON PLU=ON L4
L22 24982 SEA FILE=CAPLUS ABB=ON PLU=ON L5
L25 130 SEA FILE=CAPLUS ABB=ON PLU=ON L18 (L) PREP/RL
L26 3070185 SEA FILE=CAPLUS ABB=ON PLU=ON (RACT OR RCT OR RGT)/RL
L27 2588 SEA FILE=CAPLUS ABB=ON PLU=ON L21 (L) L26
L28 9152 SEA FILE=CAPLUS ABB=ON PLU=ON L22 (L) L26
L29 32 SEA FILE=CAPLUS ABB=ON PLU=ON L27 AND L28 AND L25
L64 1462878 SEA FILE=CAPLUS ABB=ON PLU=ON ?CATALY?/BI
L66 32 SEA FILE=CAPLUS ABB=ON PLU=ON L64 AND L29

=> d stat que L84
L2 1 SEA FILE=REGISTRY ABB=ON PLU=ON 4635-87-4
L4 1 SEA FILE=REGISTRY ABB=ON PLU=ON 74-90-8
L5 1 SEA FILE=REGISTRY ABB=ON PLU=ON 106-99-0
L9 2 SEA FILE=REGISTRY ABB=ON PLU=ON "3-PENTENENITRILE, ("?/CN
L10 3 SEA FILE=REGISTRY ABB=ON PLU=ON L2 OR L9
L11 2 SEA FILE=REGISTRY ABB=ON PLU=ON (16529-66-1/CRN OR 16545-78-1
/CRN OR 4635-87-4/CRN)
L13 5 SEA FILE=REGISTRY ABB=ON PLU=ON L10 OR L11
L17 1 SEA FILE=REGISTRY ABB=ON PLU=ON "3-PENTENENITRILE-2,2-D2"/CN

L18 6 SEA FILE=REGISTRY ABB=ON PLU=ON L13 OR L17
L21 17208 SEA FILE=CAPLUS ABB=ON PLU=ON L4
L22 24982 SEA FILE=CAPLUS ABB=ON PLU=ON L5
L23 383 SEA FILE=CAPLUS ABB=ON PLU=ON L18
L24 47 SEA FILE=CAPLUS ABB=ON PLU=ON L21 AND L22 AND L23
L76 1 SEA FILE=REGISTRY ABB=ON PLU=ON NITROGEN/CN
L77 1 SEA FILE=REGISTRY ABB=ON PLU=ON HELIUM/CN
L78 1 SEA FILE=REGISTRY ABB=ON PLU=ON ARGON/CN
L79 1 SEA FILE=REGISTRY ABB=ON PLU=ON KRYPTON/CN
L80 1 SEA FILE=REGISTRY ABB=ON PLU=ON NEON/CN
L81 1 SEA FILE=REGISTRY ABB=ON PLU=ON XENON/CN
L82 1 SEA FILE=REGISTRY ABB=ON PLU=ON RADON/CN
L83 1 SEA FILE=REGISTRY ABB=ON PLU=ON AIR/CN
L84 2 SEA FILE=CAPLUS ABB=ON PLU=ON L24 AND (L76 OR L77 OR L78 OR
L79 OR L80 OR L81 OR L82 OR L83)

=> s L40 or L41 or L42 or L61 or L63 or L66 or L84
L86 34 L40 OR L41 OR L42 OR L61 OR L63 OR L66 OR L84

=> file casreact
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FILE CONTENT:1840 - 26 Jan 2008 VOL 148 ISS 5

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*****
*          CASREACT now has more than 13.8 million reactions      *
*****
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This file contains CAS Registry Numbers for easy and accurate substance identification.

```
=> d stat que L72
L2      1 SEA FILE=REGISTRY ABB=ON   PLU=ON  4635-87-4
L9      2 SEA FILE=REGISTRY ABB=ON   PLU=ON  "3-PENTENENITRILE, ("?/CN
L10     3 SEA FILE=REGISTRY ABB=ON   PLU=ON  L2 OR L9
L11     2 SEA FILE=REGISTRY ABB=ON   PLU=ON  (16529-66-1/CRN OR 16545-78-1
      /CRN OR 4635-87-4/CRN)
L13     5 SEA FILE=REGISTRY ABB=ON   PLU=ON  L10 OR L11
L17     1 SEA FILE=REGISTRY ABB=ON   PLU=ON  "3-PENTENENITRILE-2,2-D2"/CN

L18      6 SEA FILE=REGISTRY ABB=ON   PLU=ON  L13 OR L17
L68     39 SEA FILE=CASREACT ABB=ON  PLU=ON  L18/PRO
L69     723 SEA FILE=CASREACT ABB=ON PLU=ON  74-90-8
L70    1995 SEA FILE=CASREACT ABB=ON PLU=ON  106-99-0
L71     16 SEA FILE=CASREACT ABB=ON PLU=ON  L68 (L) L69
L72     15 SEA FILE=CASREACT ABB=ON PLU=ON  L71 (L) L70
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```
=> file uspatfull
FILE 'USPATFULL' ENTERED AT 15:34:03 ON 01 FEB 2008
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FILE COVERS 1971 TO PATENT PUBLICATION DATE: 31 Jan 2008 (20080131/PD)
FILE LAST UPDATED: 31 Jan 2008 (20080131/ED)
HIGHEST GRANTED PATENT NUMBER: US7325253
HIGHEST APPLICATION PUBLICATION NUMBER: US2008028492
CA INDEXING IS CURRENT THROUGH 31 Jan 2008 (20080131/UPCA)
ISSUE CLASS FIELDS (/INCL) CURRENT THROUGH: 31 Jan 2008 (20080131/PD)
REVISED CLASS FIELDS (/NCL) LAST RELOADED: Dec 2007
USPTO MANUAL OF CLASSIFICATIONS THESAURUS ISSUE DATE: Dec 2007

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=> d stat que L44
L2      1 SEA FILE=REGISTRY ABB=ON   PLU=ON  4635-87-4
L4      1 SEA FILE=REGISTRY ABB=ON   PLU=ON  74-90-8
L5      1 SEA FILE=REGISTRY ABB=ON   PLU=ON  106-99-0
L9      2 SEA FILE=REGISTRY ABB=ON   PLU=ON  "3-PENTENENITRILE, ("?/CN
L10     3 SEA FILE=REGISTRY ABB=ON   PLU=ON  L2 OR L9
L11     2 SEA FILE=REGISTRY ABB=ON   PLU=ON  (16529-66-1/CRN OR 16545-78-1
      /CRN OR 4635-87-4/CRN)
L13     5 SEA FILE=REGISTRY ABB=ON   PLU=ON  L10 OR L11
L17     1 SEA FILE=REGISTRY ABB=ON   PLU=ON  "3-PENTENENITRILE-2,2-D2"/CN
```

L18 6 SEA FILE=REGISTRY ABB=ON PLU=ON L13 OR L17
L30 297092 SEA FILE=CAPLUS ABB=ON PLU=ON ?POROUS?/BI
L31 40403 SEA FILE=CAPLUS ABB=ON PLU=ON MICROPOR?/BI
L32 30953 SEA FILE=CAPLUS ABB=ON PLU=ON MOLECULAR SIEV?/BI
L33 128603 SEA FILE=CAPLUS ABB=ON PLU=ON ZEOLIT?/BI
L34 23369 SEA FILE=CAPLUS ABB=ON PLU=ON MESOPOR?/BI
L35 1378 SEA FILE=CAPLUS ABB=ON PLU=ON ADSORBANT?/BI
L36 375297 SEA FILE=CAPLUS ABB=ON PLU=ON CERAMIC?/BI
L43 24 SEA FILE=USPATFULL ABB=ON PLU=ON L4 AND L5 AND L18
L44 6 SEA FILE=USPATFULL ABB=ON PLU=ON L43 AND (L30 OR L31 OR L32
 OR L33 OR L34 OR L35 OR L36)

=> d stat que L45
L2 1 SEA FILE=REGISTRY ABB=ON PLU=ON 4635-87-4
L4 1 SEA FILE=REGISTRY ABB=ON PLU=ON 74-90-8
L5 1 SEA FILE=REGISTRY ABB=ON PLU=ON 106-99-0
L9 2 SEA FILE=REGISTRY ABB=ON PLU=ON "3-PENTENENITRILE, (?/CN
L10 3 SEA FILE=REGISTRY ABB=ON PLU=ON L2 OR L9
L11 2 SEA FILE=REGISTRY ABB=ON PLU=ON (16529-66-1/CRN OR 16545-78-1
 /CRN OR 4635-87-4/CRN)
L13 5 SEA FILE=REGISTRY ABB=ON PLU=ON L10 OR L11
L17 1 SEA FILE=REGISTRY ABB=ON PLU=ON "3-PENTENENITRILE-2,2-D2"/CN

L18 6 SEA FILE=REGISTRY ABB=ON PLU=ON L13 OR L17
L37 54059 SEA FILE=CAPLUS ABB=ON PLU=ON AIR/CT
L38 18350 SEA FILE=CAPLUS ABB=ON PLU=ON NOBLE GAS?/BI
L39 15276 SEA FILE=CAPLUS ABB=ON PLU=ON HELIUM GROUP?/BI
L43 24 SEA FILE=USPATFULL ABB=ON PLU=ON L4 AND L5 AND L18
L45 2 SEA FILE=USPATFULL ABB=ON PLU=ON L43 AND (L37 OR L38 OR L39)

=> d stat que L48
L2 1 SEA FILE=REGISTRY ABB=ON PLU=ON 4635-87-4
L4 1 SEA FILE=REGISTRY ABB=ON PLU=ON 74-90-8
L5 1 SEA FILE=REGISTRY ABB=ON PLU=ON 106-99-0
L9 2 SEA FILE=REGISTRY ABB=ON PLU=ON "3-PENTENENITRILE, (?/CN
L10 3 SEA FILE=REGISTRY ABB=ON PLU=ON L2 OR L9
L11 2 SEA FILE=REGISTRY ABB=ON PLU=ON (16529-66-1/CRN OR 16545-78-1
 /CRN OR 4635-87-4/CRN)
L13 5 SEA FILE=REGISTRY ABB=ON PLU=ON L10 OR L11
L17 1 SEA FILE=REGISTRY ABB=ON PLU=ON "3-PENTENENITRILE-2,2-D2"/CN

L18 6 SEA FILE=REGISTRY ABB=ON PLU=ON L13 OR L17
L43 24 SEA FILE=USPATFULL ABB=ON PLU=ON L4 AND L5 AND L18
L47 250630 SEA FILE=USPATFULL ABB=ON PLU=ON HELIUM OR ARGON OR NEON OR
 KRYPTON OR XENON OR RADON
L48 14 SEA FILE=USPATFULL ABB=ON PLU=ON L47 AND L43

=> d stat que L51
L2 1 SEA FILE=REGISTRY ABB=ON PLU=ON 4635-87-4
L4 1 SEA FILE=REGISTRY ABB=ON PLU=ON 74-90-8
L5 1 SEA FILE=REGISTRY ABB=ON PLU=ON 106-99-0
L9 2 SEA FILE=REGISTRY ABB=ON PLU=ON "3-PENTENENITRILE, (?/CN
L10 3 SEA FILE=REGISTRY ABB=ON PLU=ON L2 OR L9
L11 2 SEA FILE=REGISTRY ABB=ON PLU=ON (16529-66-1/CRN OR 16545-78-1
 /CRN OR 4635-87-4/CRN)

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L13 5 SEA FILE=REGISTRY ABB=ON PLU=ON L10 OR L11
L17 1 SEA FILE=REGISTRY ABB=ON PLU=ON "3-PENTENENITRILE-2,2-D2"/CN

L18 6 SEA FILE=REGISTRY ABB=ON PLU=ON L13 OR L17
L43 24 SEA FILE=USPATFULL ABB=ON PLU=ON L4 AND L5 AND L18
L50 1664593 SEA FILE=USPATFULL ABB=ON PLU=ON AIR OR NITROGEN
L51 15 SEA FILE=USPATFULL ABB=ON PLU=ON L43 AND L50

=> d stat que L57
L2 1 SEA FILE=REGISTRY ABB=ON PLU=ON 4635-87-4
L4 1 SEA FILE=REGISTRY ABB=ON PLU=ON 74-90-8
L5 1 SEA FILE=REGISTRY ABB=ON PLU=ON 106-99-0
L9 2 SEA FILE=REGISTRY ABB=ON PLU=ON "3-PENTENENITRILE, (?/CN
L10 3 SEA FILE=REGISTRY ABB=ON PLU=ON L2 OR L9
L11 2 SEA FILE=REGISTRY ABB=ON PLU=ON (16529-66-1/CRN OR 16545-78-1
/CRN OR 4635-87-4/CRN)
L13 5 SEA FILE=REGISTRY ABB=ON PLU=ON L10 OR L11
L17 1 SEA FILE=REGISTRY ABB=ON PLU=ON "3-PENTENENITRILE-2,2-D2"/CN

L18 6 SEA FILE=REGISTRY ABB=ON PLU=ON L13 OR L17
L25 130 SEA FILE=CAPLUS ABB=ON PLU=ON L18 (L) PREP/RL
L43 24 SEA FILE=USPATFULL ABB=ON PLU=ON L4 AND L5 AND L18
L53 485246 SEA FILE=USPATFULL ABB=ON PLU=ON CATALY?
L54 24 SEA FILE=USPATFULL ABB=ON PLU=ON L43 AND L53
L55 TRANSFER PLU=ON L25 1- PN : 646 TERMS
L56 56 SEA FILE=USPATFULL ABB=ON PLU=ON L55
L57 18 SEA FILE=USPATFULL ABB=ON PLU=ON L56 AND L54

=> s L44 or L45 or L48 or L51 or L57
L87 24 L44 OR L45 OR L48 OR L51 OR L57

=> file stnguide
FILE 'STNGUIDE' ENTERED AT 15:35:01 ON 01 FEB 2008
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FILE CONTAINS CURRENT INFORMATION.
LAST RELOADED: Jan 25, 2008 (20080125/UP).

=> dup rem L86 L72 L87
FILE 'CAPLUS' ENTERED AT 15:35:24 ON 01 FEB 2008
USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.
PLEASE SEE "HELP USAGETERMS" FOR DETAILS.
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FILE 'CASREACT' ENTERED AT 15:35:24 ON 01 FEB 2008
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FILE 'USPATFULL' ENTERED AT 15:35:24 ON 01 FEB 2008
CA INDEXING COPYRIGHT (C) 2008 AMERICAN CHEMICAL SOCIETY (ACS)
PROCESSING COMPLETED FOR L86
PROCESSING COMPLETED FOR L72
PROCESSING COMPLETED FOR L87
L88 60 DUP REM L86 L72 L87 (13 DUPLICATES REMOVED)
ANSWERS '1-34' FROM FILE CAPLUS
ANSWERS '35-37' FROM FILE CASREACT
ANSWERS '38-60' FROM FILE USPATFULL

=> d ibib abs hitind hitstr L88 1-34; d ibib abs hit L88 35-37; d ibib abs kwic hit
hitstr L88 38-60

L88 ANSWER 1 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN DUPLICATE 1
 ACCESSION NUMBER: 2005:729622 CAPLUS Full-text
 DOCUMENT NUMBER: 143:195585
 TITLE: Catalytic hydrocyanation production of
 3-pentenenitrile from 1,3-butadiene and hydrogen
 cyanide
 INVENTOR(S): Scheidel, Jens; Jungkamp, Tim; Bartsch, Michael;
 Haderlein, Gerd; Baumann, Robert; Luyken, Hermann
 PATENT ASSIGNEE(S): BASF Aktiengesellschaft, Germany
 SOURCE: PCT Int. Appl., 48 pp.
 CODEN: PIXKD2
 DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|--|------|----------|-----------------------|------------|
| WO 2005073175 | A1 | 20050811 | WO 2005-EP'84 | 20050127 |
| W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW | | | | |
| RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG | | | | |
| DE 102004004724 | A1 | 20050818 | DE 2004-102004004724 | 20040129 |
| CA 2552862 | A1 | 20050811 | CA 2005-2552862 | 20050127 |
| EP 1716106 | A1 | 20061102 | EP 2005-707030 | 20050127 |
| R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, FI, RO, CY, TR, BG, CZ, EE, HU, PL, SK, IS | | | | |
| CN 1914161 | A | 20070214 | CN 2005-80003699 | 20050127 |
| BR 2005007129 | A | 20070619 | BR 2005-7129 | 20050127 |
| JP 2007519677 | T | 20070719 | JP 2006-550103 | 20050127 |
| MX 2006PA07886 | A | 20061002 | MX 2006-PA'886 | 20060710 |
| KR 2007011277 | A | 20070124 | KR 2006-715314 | 20060728 |
| IN 2006CN03125 | A | 20070608 | IN 2006-CN3125 | 20060829 |
| PRIORITY APPLN. INFO.: | | | DE 2004-102004004724A | 20040129 |
| | | | WO 2005-EP'784 | W 20050127 |

OTHER SOURCE(S): CASREACT 143:195585

- AB A method is described for producing 3-pentenenitrile by means of the hydrocyanation of 1,3-butadiene, where 1,3-butadiene is reacted with hydrogen cyanide in the presence of at least one Ni-phosphorus ligand complex catalyst, and the resulting flow is purified by distillation, the bottom temperature not exceeding 140° during the distillation. Process flow diagrams are presented.
- IC ICM C07C253-10
 ICS C07C255-07
- CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)
 Section cross-reference(s): 23, 48, 67
- ST pentenenitrile manuf catalytic hydrocyanation butadiene distn
- IT Alkadienes
- RL: EPR (Engineering process); PEP (Physical, engineering or chemical

process); RCT (Reactant); PROC (Process); RACT (Reactant or reagent)
 (1,3-butadiene; catalytic hydrocyanation production of
 3-pentenenitrile from 1,3-butadiene and hydrogen cyanide)

IT Hydrocyanation catalysts
 (Ni-phosphorus ligand complexes; catalytic hydrocyanation
 production of 3-pentenenitrile from 1,3-butadiene and hydrogen cyanide)

IT Hydrocyanation
 (catalytic hydrocyanation production of 3-pentenenitrile from
 1,3-butadiene and hydrogen cyanide)

IT Distillation
 Distillation apparatus
 Distillation columns
 (in the catalytic hydrocyanation production of 3-pentenenitrile
 from 1,3-butadiene and hydrogen cyanide)

IT Phosphites
 RL: CAT (Catalyst use); EPR (Engineering process); PEP (Physical,
 engineering or chemical process); PROC (Process); USES (Uses)
 (ligands; in the catalytic hydrocyanation production of
 3-pentenenitrile from 1,3-butadiene and hydrogen cyanide)

IT Nitriles, preparation
 RL: EPR (Engineering process); IMF (Industrial manufacture); PEP
 (Physical, engineering or chemical process); PREP (Preparation); PROC
 (Process)
 (unsatd., 3-pentenenitriles; catalytic hydrocyanation production
 of 3-pentenenitrile from 1,3-butadiene and hydrogen cyanide)

IT 4635-87-4F, 3-Pentenenitrile
 RL: EPR (Engineering process); IMF (Industrial manufacture); PEP
 (Physical, engineering or chemical process); PREP (Preparation);
 PROC (Process)
 (catalytic hydrocyanation production of 3-pentenenitrile from
 1,3-butadiene and hydrogen cyanide)

IT 590-18-1, cis-2-Butene
 RL: EPR (Engineering process); NUU (Other use, unclassified); PEP
 (Physical, engineering or chemical process); PROC (Process); USES (Uses)
 (catalytic hydrocyanation production of 3-pentenenitrile from
 1,3-butadiene and hydrogen cyanide)

IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,
 1,3-Butadiene, reactions 16529-66-1, trans-3-Pentenenitrile
 16545-78-1, cis-3-Pentenenitrile
 RL: EPR (Engineering process); PEP (Physical, engineering or chemical
 process); RCT (Reactant); PROC (Process); RACT (Reactant or
 reagent)
 (catalytic hydrocyanation production of 3-pentenenitrile from
 1,3-butadiene and hydrogen cyanide)

IT 1295-35-8 220472-84-4 509083-87-8
 RL: CAT (Catalyst use); EPR (Engineering process); PEP (Physical,
 engineering or chemical process); PROC (Process); USES (Uses)
 (ligand; catalytic hydrocyanation production of 3-pentenenitrile
 from 1,3-butadiene and hydrogen cyanide)

IT 4635-87-4P, 3-Pentenenitrile
 RL: EPR (Engineering process); IMF (Industrial manufacture); PEP
 (Physical, engineering or chemical process); PREP (Preparation);
 PROC (Process)
 (catalytic hydrocyanation production of 3-pentenenitrile from
 1,3-butadiene and hydrogen cyanide)

RN 4635-87-4 CAPLUS

CN 3-Pentenenitrile (CA INDEX NAME)



IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,
1,3-Butadiene, reactions
RL: EPR (Engineering process); PEP (Physical, engineering or chemical
process); RCT (Reactant); PROC (Process); RACT (Reactant or
reagent)
(catalytic hydrocyanation production of 3-pentenenitrile from
1,3-butadiene and hydrogen cyanide)

RN 74-90-8 CAPLUS
CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 CAPLUS
CN 1,3-Butadiene (CA INDEX NAME)



REFERENCE COUNT: 1 THERE ARE 1 CITED REFERENCES AVAILABLE FOR THIS
RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L88 ANSWER 2 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN DUPLICATE 2
ACCESSION NUMBER: 2005:729621 CAPLUS Full-text
DOCUMENT NUMBER: 143:195584
TITLE: Manufacture of linear 3-pentenenitrile from streams
containing 2-methyl-3-butenenitrile
INVENTOR(S): Jungkamp, Tim; Baumann, Robert; Bartsch, Michael;
Haderlein, Gerd; Luyken, Hermann; Scheidel, Jens;
Aechtner, Tobias; Pfab, Peter; Deckert, Petra
PATENT ASSIGNEE(S): BASF Aktiengesellschaft, Germany
SOURCE: PCT Int. Appl., 116 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|--|------|----------|-----------------|----------|
| WO 2005073174 | A1 | 20050811 | WO 2005-EP781 | 20050127 |
| W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW | | | | |

RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG

| | | | | |
|---|----|----------|-----------------------|------------|
| DE 102004004671 | A1 | 20050818 | DE 2004-102004004671 | 20040129 |
| DE 102004042949 | A1 | 20060309 | DE 2004-102004042949 | 20040902 |
| DE 102004063381 | A1 | 20060706 | DE 2004-102004063381 | 20041223 |
| CA 2554736 | A1 | 20050811 | CA 2005-2554736 | 20050127 |
| EP 1716105 | A1 | 20061102 | EP 2005-707029 | 20050127 |
| R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, FI, RO, CY, TR, BG, CZ, EE, HU, PL, SK, IS | | | | |
| CN 1914159 | A | 20070214 | CN 2005-80003693 | 20050127 |
| BR 200507197 | A | 20070626 | BR 2005-7197 | 20050127 |
| JP 2007519675 | T | 20070719 | JP 2006-550101 | 20050127 |
| MX 2006PA07813 | A | 20060926 | MX 2006-PA7813 | 20060707 |
| IN 2006CN03134 | A | 20070608 | IN 2006-CN3134 | 20060829 |
| PRIORITY APPLN. INFO.: | | | | |
| | | | DE 2004-102004004671A | 20040129 |
| | | | DE 2004-102004042949A | 20040902 |
| | | | DE 2004-102004063381A | 20041223 |
| | | | WO 2005-EP781 | W 20050127 |

OTHER SOURCE(S): CASREACT 143:195584; MARPAT 143:195584

AB The title compound, an adiponitrile intermediate useful for the manufacture of polyamides, is manufactured by (A) isomerization of an educt stream containing 2-methyl-3-butenenitrile obtained by hydrocyanation of 1,3-butadiene on ≥ 1 dissolved or dispersed isomerization catalyst to form a stream (1), which contains the isomerization catalyst(s), 2-methyl-3- butenenitrile, 3-pentenenitrile and (Z)-2-methyl-2-butenenitrile; (B) distillation of the stream (1) to obtain a stream (2) as the overhead product, which contains 2-methyl-3-butenenitrile, 3-pentenenitrile and (Z)-2-methyl-2-butenenitrile and a stream (3) as the bottom product, which contains the isomerization catalyst(s), (C) distillation of the stream (2) to obtain a stream (4) as the overhead product, which is enriched with (Z)-2-methyl-2-butenenitrile in comparison to stream (2), [in relation to the sum of all pentenenitriles in stream (2)] and a stream (5) as the bottom product, which is enriched with 3-pentenenitrile and 2-methyl-3-butenenitrile in comparison to stream (2), [in relation to the sum of all pentenenitriles in stream (2)], (D) distillation of stream (5) to obtain a stream (6) as the bottom product, which contains 3-pentenenitrile and a stream (7) as the head product, which contains 2-methyl-3- butenenitrile. The process is exemplified by use of block schematic diagrams.

IC ICM C07C253-10

ICS C07C255-07

CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)

IT Distillation

Hydrocyanation catalysts

Isomerization

(manufacture of linear pentenenitrile from streams containing methylbutenenitrile)

IT Isomerization catalysts

(nickel compds. with o-isopropylphenyl-m/p-tolyl phosphites; manufacture of linear pentenenitrile from streams containing methylbutenenitrile)

IT 7440-02-0D, Nickel, compds. with P-containing ligands 25586-42-9D, Tritolyl phosphite, nickel complexes 509083-87-8D, nickel complexes 861509-78-6D, nickel complexes

RL: CAT (Catalyst use); USES (Uses)

(hydrocyanation catalysts; manufacture of linear pentenenitrile from streams containing methylbutenenitrile)

IT 74-90-3, Hydrogen cyanide, reactions

RL: PCT (Reactant); PACT (Reactant or reagent)

10/586490

(hydrocyanation of butadiene; manufacture of linear pentenenitrile from streams containing methylbutenenitrile)

IT 106-99-0, 1,3-Butadiene, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(hydrocyanation; manufacture of linear pentenenitrile from streams containing methylbutenenitrile)

IT 4635-87-4E, 3-Pentenenitrile
RL: IMF (Industrial manufacture); PEP (Physical, engineering or chemical process); PYP (Physical process); PREP (Preparation); PROC (Process)
(manufacture of linear pentenenitrile from streams containing methylbutenenitrile)

IT 74-90-8, Hydrogen cyanide, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(hydrocyanation of butadiene; manufacture of linear pentenenitrile from streams containing methylbutenenitrile)

RN 74-90-8 CAPLUS

CN Hydrocyanic acid (CA INDEX NAME)



IT 106-99-0, 1,3-Butadiene, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(hydrocyanation; manufacture of linear pentenenitrile from streams containing methylbutenenitrile)

RN 106-99-0 CAPLUS

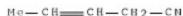
CN 1,3-Butadiene (CA INDEX NAME)



IT 4635-87-4E, 3-Pentenenitrile
RL: IMF (Industrial manufacture); PEP (Physical, engineering or chemical process); PYP (Physical process); PREP (Preparation); PROC (Process)
(manufacture of linear pentenenitrile from streams containing methylbutenenitrile)

RN 4635-87-4 CAPLUS

CN 3-Pentenenitrile (CA INDEX NAME)



REFERENCE COUNT: 3 THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L88 ANSWER 3 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN DUPLICATE 3

ACCESSION NUMBER: 2005:729620 CAPLUS Full-text

DOCUMENT NUMBER: 143:195583

TITLE: Method for the hydrocyanation of 1,3-butadiene into 3-pentenenitrile using a loop-type bubble column reactor comprising an external pumping circuit and a jet nozzle for driving the inner circulation

INVENTOR(S): Jungkamp, Tim; Baumann, Robert; Bartsch, Michael; Haderlein, Gerd; Luyken, Hermann; Scheidel, Jens

PATENT ASSIGNEE(S): BASF Aktiengesellschaft, Germany

SOURCE: PCT Int. Appl., 24 pp.

CODEN: PIXKD2

DOCUMENT TYPE: Patent

LANGUAGE: German

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|--|------|----------|-----------------------|------------|
| WO 2005073173 | A1 | 20050811 | WO 2005-EP780 | 20050127 |
| W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA,UG, US, UZ, VC, VN, YU, ZA, ZM, ZW | | | | |
| RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG | | | | |
| DE 102004004673 | A1 | 20050818 | DE 2004-102004004673 | 20040129 |
| EP 1713762 | A1 | 20061025 | EP 2005-707028 | 20050127 |
| R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, FI, RO, CY, TR, BG, CZ, EE, HU, PL, SK, IS | | | | |
| CN 1914155 | A | 20070214 | CN 2005-80003622 | 20050127 |
| JP 2007519674 | T | 20070719 | JP 2006-550100 | 20050127 |
| PRIORITY APPLN. INFO.: | | | DE 2004-102004004673A | 20040129 |
| | | | WO 2005-EP780 | W 20050127 |

OTHER SOURCE(S): CASREACT 143:195583

AB A method for producing 3-pentenenitrile by means of the hydrocyanation of 1,3-butadiene in the presence of at least one catalyst is described where the hydrocyanation reaction is carried out in a loop-type bubble reactor column comprising an external pumping circuit and a jet nozzle for driving the inner circulation.

IC ICM C07C253-10

ICS C07C255-07

CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)

Section cross-reference(s): 23, 48

ST pentenenitrile manuf catalytic hydrocyanation butadiene loop type reactor

IT Hydrocyanation

Hydrocyanation catalysts

(method for the hydrocyanation of 1,3-butadiene into 3-pentenenitrile using a loop-type bubble column reactor comprising an external pumping circuit and a jet nozzle for driving the inner circulation)

IT 4635-87-4P, 3-Pentenenitrile

RL: IMF (Industrial manufacture); PREP (Preparation)

(method for the hydrocyanation of 1,3-butadiene into 3-pentenenitrile using a loop-type bubble column reactor comprising an external pumping circuit and a jet nozzle for driving the inner circulation)

10/586490

IT 74-90-3, Hydrogen cyanide, reactions 106-99-0,
1,3-Butadiene, reactions
RL: PCT (Reactant); PACT (Reactant or reagent)
(method for the hydrocyanation of 1,3-butadiene into 3-pentenenitrile
using a loop-type bubble column reactor comprising an external pumping
circuit and a jet nozzle for driving the inner circulation)
IT 4635-87-4, 3-Pentenenitrile
RL: IMF (Industrial manufacture); PREP (Preparation)
(method for the hydrocyanation of 1,3-butadiene into 3-pentenenitrile
using a loop-type bubble column reactor comprising an external pumping
circuit and a jet nozzle for driving the inner circulation)
RN 4635-87-4 CAPLUS
CN 3-Pentenenitrile (CA INDEX NAME)



IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,
1,3-Butadiene, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(method for the hydrocyanation of 1,3-butadiene into 3-pentenenitrile
using a loop-type bubble column reactor comprising an external pumping
circuit and a jet nozzle for driving the inner circulation)
RN 74-90-8 CAPLUS
CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 CAPLUS
CN 1,3-Butadiene (CA INDEX NAME)



REFERENCE COUNT: 3 THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS
RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L98 ANSWER 4 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN DUPLICATE 4
ACCESSION NUMBER: 2005:729618 CAPLUS Full-text
DOCUMENT NUMBER: 143:195581
TITLE: Catalytic hydrocyanation method for producing
3-pentenenitrile from hydrogen cyanide and
1,3-butadiene
INVENTOR(S): Scheidel, Jens; Jungkamp, Tim; Bartsch, Michael;
Haderlein, Gerd; Baumann, Robert; Luyken, Hermann
PATENT ASSIGNEE(S): BASF Aktiengesellschaft, Germany
SOURCE: PCT Int. Appl., 55 pp.
CODEN: PIXXD2

DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|--|------|----------|-----------------------|------------|
| WO 2005073171 | A1 | 20050811 | WO 2005-EP774 | 20050127 |
| W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW | | | | |
| RW: BW, GH, GM, KE, LS, MW, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG | | | | |
| DE 102004004720 | A1 | 20050818 | DE 2004-102004004720 | 20040129 |
| CA 2552860 | A1 | 20050811 | CA 2005-2552860 | 20050127 |
| EP 1716104 | A1 | 20061102 | EP 2005-701203 | 20050127 |
| R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, FI, RO, CY, TR, BG, CZ, EE, HU, PL, SK, IS | | | | |
| CN 1914154 | A | 20070214 | CN 2005-80003621 | 20050127 |
| BR 2005006587 | A | 20070502 | BR 2005-6587 | 20050127 |
| JP 2007519672 | T | 20070719 | JP 2006-550097 | 20050127 |
| MX 2006PA07883 | A | 20061002 | MX 2006-PA7883 | 20060710 |
| KR 2007011278 | A | 20070124 | KR 2006-715315 | 20060728 |
| IN 2006CN03123 | A | 20070608 | IN 2006-CN3123 | 20060829 |
| PRIORITY APPLN. INFO.: | | | DE 2004-102004004720A | 20040129 |
| | | | WO 2005-EP774 | W 20050127 |

OTHER SOURCE(S): CASREACT 143:195581

AB A method is described for producing 3-pentenenitrile comprising: (a) 1,3-butadiene is reacted with hydrogen cyanide over at least one catalyst to obtain a flow (1) containing 3-pentenenitrile, 2-methyl-3-butenenitrile, the catalyst, and 1,3-butadiene; (b) the flow (1) is distilled in a column to obtain a head product flow (2) rich in 1,3-butadiene, and a bottom product flow (3) that is poor in 1,3-butadiene and contains 3-pentenenitrile, the catalyst, and 2-methyl-3-butenenitrile; (c) the flow (3) is distilled in a column to obtain a head product flow (4) containing 1,3-butadiene, a flow (5) in a side-tap of the column, containing 3-pentenenitrile and 2-methyl-3-butenenitrile, and a bottom product flow (6) containing the catalyst; and (d) the flow (5) is distilled to obtain a head product flow (7) containing 2-methyl-3-butenenitrile and a bottom product flow (8) containing 3-pentenenitrile. Process flow diagrams are presented.

IC ICM C07C253-10

ICS C07C253-34; C07C255-07

CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)

Section cross-reference(s): 23, 48, 67

ST pentenenitrile manuf catalytic hydrocyanation butadiene

IT Alkadienes

RL: EPR (Engineering process); PEP (Physical, engineering or chemical process); RCT (Reactant); PROC (Process); RACT (Reactant or reagent)
 (1,3-butadiene; catalytic hydrocyanation method for producing
 3-pentenenitrile from hydrogen cyanide and 1,3-butadiene)

IT Hydrocyanation

(catalytic hydrocyanation method for producing
 3-pentenenitrile from hydrogen cyanide and 1,3-butadiene)

IT Hydrocyanation catalysts

- (elemental Ni-phosphine complexes; catalytic hydrocyanation method for producing 3-pentenenitrile from hydrogen cyanide and 1,3-butadiene)
- IT Distillation
 Distillation apparatus
 Distillation columns
 Isomerization
 Isomerization catalysts
 Process control
 (in a catalytic hydrocyanation method for producing 3-pentenenitrile from hydrogen cyanide and 1,3-butadiene)
- IT Phosphines
 Phosphites
 Phosphonates
 RL: CAT (Catalyst use); EPR (Engineering process); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses)
 (ligands; in a catalytic hydrocyanation method for producing 3-pentenenitrile from hydrogen cyanide and 1,3-butadiene)
- IT Nitriles, preparation
 RL: EPR (Engineering process); IMF (Industrial manufacture); PEP (Physical, engineering or chemical process); PREP (Preparation); PROC (Process)
 (unsaat., 3-pentenenitriles; catalytic hydrocyanation method for producing 3-pentenenitrile from hydrogen cyanide and 1,3-butadiene)
- IT 592-51-8P, 4-Pentenenitrile 26294-98-4P, trans-2-Pentenenitrile
 RL: BYP (Byproduct); EPR (Engineering process); PEP (Physical, engineering or chemical process); PREP (Preparation); PROC (Process)
 (catalytic hydrocyanation method for producing 3-pentenenitrile from hydrogen cyanide and 1,3-butadiene)
- IT 7440-02-0, Nickel, uses
 RL: CAT (Catalyst use); USES (Uses)
 (catalytic hydrocyanation method for producing 3-pentenenitrile from hydrogen cyanide and 1,3-butadiene)
- IT 220472-84-4 509083-87-8
 RL: CAT (Catalyst use); EPR (Engineering process); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses)
 (catalytic hydrocyanation method for producing 3-pentenenitrile from hydrogen cyanide and 1,3-butadiene)
- IT 16529-66-1P 16545-78-1P, cis-3-Pentenenitrile
 25899-50-7P, cis-2-Pentenenitrile
 RL: EPR (Engineering process); IMF (Industrial manufacture); PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PREP (Preparation); PROC (Process)
 (catalytic hydrocyanation method for producing 3-pentenenitrile from hydrogen cyanide and 1,3-butadiene)
- IT 4615-87-4P, 3-Pentenenitrile
 RL: EPR (Engineering process); IMF (Industrial manufacture); PEP (Physical, engineering or chemical process); PYP (Physical process); PREP (Preparation); PROC (Process)
 (catalytic hydrocyanation method for producing 3-pentenenitrile from hydrogen cyanide and 1,3-butadiene)
- IT 16529-56-9P, 2-Methyl-3-butenenitrile
 RL: EPR (Engineering process); IMF (Industrial manufacture); PEP (Physical, engineering or chemical process); PYP (Physical process); RCT (Reactant); PREP (Preparation); PROC (Process); RACT (Reactant or reagent)
 (catalytic hydrocyanation method for producing 3-pentenenitrile from hydrogen cyanide and 1,3-butadiene)
- IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,
 1,3-Butadiene, reactions
 RL: EPR (Engineering process); PEP (Physical, engineering or chemical

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process); PYP (Physical process); RCT (Reactant); PROC (Process); RACT (Reactant or reagent)
(catalytic hydrocyanation method for producing
3-pentenenitrile from hydrogen cyanide and 1,3-butadiene)
IT 16529-66-1P 16545-78-1P, cis-3-Pentenenitrile
RL: EPR (Engineering process); IMF (Industrial manufacture); PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PREP (Preparation); PROC (Process)
(catalytic hydrocyanation method for producing
3-pentenenitrile from hydrogen cyanide and 1,3-butadiene)
RN 16529-66-1 CAPLUS
CN 3-Pentenenitrile, (3E)- (CA INDEX NAME)

Double bond geometry as shown.



RN 16545-78-1 CAPLUS
CN 3-Pentenenitrile, (3Z)- (CA INDEX NAME)

Double bond geometry as shown.



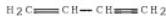
IT 4635-87-4P, 3-Pentenenitrile
RL: EPR (Engineering process); IMF (Industrial manufacture); PEP (Physical, engineering or chemical process); PYP (Physical process);
PREP (Preparation); PROC (Process)
(catalytic hydrocyanation method for producing
3-pentenenitrile from hydrogen cyanide and 1,3-butadiene)
RN 4635-87-4 CAPLUS
CN 3-Pentenenitrile (CA INDEX NAME)



IT 74-90-6, Hydrogen cyanide, reactions 106-99-0,
1,3-Butadiene, reactions
RL: EPR (Engineering process); PEP (Physical, engineering or chemical process); PYP (Physical process); RCT (Reactant); PROC (Process); RACT (Reactant or reagent)
(catalytic hydrocyanation method for producing
3-pentenenitrile from hydrogen cyanide and 1,3-butadiene)
RN 74-90-8 CAPLUS
CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 CAPLUS
 CN 1,3-Butadiene (CA INDEX NAME)



REFERENCE COUNT: 2 THERE ARE 2 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L88 ANSWER 5 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN DUPLICATE 5
 ACCESSION NUMBER: 2005:729617 CAPLUS Full-text
 DOCUMENT NUMBER: 143:195580
 TITLE: Continuous catalytic hydrocyanation method for the production of linear pentenenitriles from 1,3-butadiene and hydrogen cyanide
 INVENTOR(S): Bartsch, Michael; Baumann, Robert; Haderlein, Gerd; Scheidel, Jens; Jungkamp, Tim; Luyken, Hermann
 PATENT ASSIGNEE(S): BASF Aktiengesellschaft, Germany
 SOURCE: PCT Int. Appl., 31 pp.
 CODEN: PIXXD2
 DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|---|------|----------|-----------------------|------------|
| WO 2005073170 | A1 | 20050811 | WO 2005-EP772 | 20050127 |
| W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW | | | | |
| RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SI, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG | | | | |
| DE 102004004696 | A1 | 20050818 | DE 2004-102004004696 | 20040129 |
| CA 2553027 | A1 | 20050811 | CA 2005-2553027 | 20050127 |
| EP 1716103 | A1 | 20061102 | EP 2005-701201 | 20050127 |
| R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, FI, RO, CY, TR, BG, CZ, EE, HU, PL, SK, IS | | | | |
| CN 1914157 | A | 20070214 | CN 2005-80003675 | 20050127 |
| BR 2005007193 | A | 20070626 | BR 2005-7193 | 20050127 |
| JP 2007519671 | T | 20070719 | JP 2006-550095 | 20050127 |
| MX 2006PA07882 | A | 20061002 | MX 2006-PA7882 | 20060710 |
| IN 2006CN03128 | A | 20070608 | IN 2006-CN3128 | 20060829 |
| PRIORITY APPLN. INFO.: | | | DE 2004-102004004696A | 20040129 |
| | | | WO 2005-EP772 | W 20050127 |

OTHER SOURCE(S):

CASREACT 143:195580

- AB A method for continuous hydrocyanation of 1,3-butadiene into linear pentenenitriles in the presence of at least one elemental nickel catalyst with chelate ligands, where 1,3-butadiene and HCN are used in a molar ratio of 1.1-1.6:1, resp.
- IC ICM C07C253-10
ICS C07C255-07
- CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)
Section cross-reference(s): 23, 48, 67
- ST pentenenitrile manuf butadiene catalytic hydrocyanation
- IT Alkadienes
RL: RCT (Reactant); RACT (Reactant or reagent)
(1,3-butadiene; continuous catalytic hydrocyanation method
for the production of linear pentenenitriles from 1,3-butadiene and hydrogen cyanide)
- IT Lewis acids
RL: CAT (Catalyst use); USES (Uses)
(catalysts; continuous catalytic hydrocyanation
method for the production of linear pentenenitriles from 1,3-butadiene and hydrogen cyanide)
- IT Distillation
Process control
(in a continuous catalytic hydrocyanation method for the
production of linear pentenenitriles from 1,3-butadiene and hydrogen cyanide)
- IT Phosphines
Phosphites
Phosphonates
RL: CAT (Catalyst use); USES (Uses)
(ligands; continuous catalytic hydrocyanation method for the
production of linear pentenenitriles from 1,3-butadiene and hydrogen cyanide)
- IT Nitriles, preparation
RL: IMF (Industrial manufacture); PREP (Preparation)
(unsatd., linear pentenenitriles; continuous catalytic
hydrocyanation method for the production of linear pentenenitriles from
1,3-butadiene and hydrogen cyanide)
- IT 16529-56-9P, 2-Methyl-3-butenenitrile
RL: BYP (Byproduct); PREP (Preparation)
(continuous catalytic hydrocyanation method for the production of
linear pentenenitriles from 1,3-butadiene and hydrogen cyanide)
- IT 1295-35-8, Bis(cyclooctadienyl)nickel 7440-02-0, Nickel, uses
7646-85-7, Zinc chloride, uses 220472-84-4 509083-87-8 509095-18-5
851024-54-9
RL: CAT (Catalyst use); USES (Uses)
(continuous catalytic hydrocyanation method for the production of
linear pentenenitriles from 1,3-butadiene and hydrogen cyanide)
- IT 4635-87-4F, 3-Pentenenitrile
RL: IMF (Industrial manufacture); PREP (Preparation)
(continuous catalytic hydrocyanation method for the production of
linear pentenenitriles from 1,3-butadiene and hydrogen cyanide)
- IT 74-90-3, Hydrogen cyanide, reactions 106-99-0,
1,3-Butadiene, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(continuous catalytic hydrocyanation method for the production of
linear pentenenitriles from 1,3-butadiene and hydrogen cyanide)
- IT 4635-87-4F, 3-Pentenenitrile
RL: IMF (Industrial manufacture); PREP (Preparation)
(continuous catalytic hydrocyanation method for the production of
linear pentenenitriles from 1,3-butadiene and hydrogen cyanide)

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RN 4635-87-4 CAPLUS
CN 3-Pentenenitrile (CA INDEX NAME)



IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,
1,3-Butadiene, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(continuous catalytic hydrocyanation method for the production of
linear pentenenitriles from 1,3-butadiene and hydrogen cyanide)
RN 74-90-8 CAPLUS
CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 CAPLUS
CN 1,3-Butadiene (CA INDEX NAME)



REFERENCE COUNT: 2 THERE ARE 2 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L88 ANSWER 6 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN DUPLICATE 6
ACCESSION NUMBER: 2005:729616 CAPLUS Full-text
DOCUMENT NUMBER: 143:195579
TITLE: Process control in a catalytic hydrocyanation method
for the conversion of 1,3-butadiene and hydrogen
cyanide into 3-pentenenitrile
INVENTOR(S): Jungkamp, Tim; Baumann, Robert; Schroeder, Thorsten;
Bartsch, Michael; Haderlein, Gerd; Luyken, Hermann;
Scheidel, Jens
PATENT ASSIGNEE(S): BASF Aktiengesellschaft, Germany
SOURCE: PCT Int. Appl., 28 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|---------------|------|----------|-----------------|----------|
| WO 2005073169 | A1 | 20050811 | WO 2005-EP725 | 20050126 |

W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH,
CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD,
GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,

LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI,
 NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY,
 TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW
 RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM,
 AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK,
 EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT,
 RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML,
 MR, NE, SN, TD, TG

| | | | | |
|--|----|----------|----------------------|----------|
| DE 102004004672 | A1 | 20050818 | DE 2004-102004004672 | 20040129 |
| CA 2553241 | A1 | 20050811 | CA 2005-2553241 | 20050126 |
| EP 1716107 | A1 | 20061102 | EP 2005-715210 | 20050126 |
| R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, FI, RO, CY, TR, BG, CZ, EE, HU, PL, SK, IS | | | | |
| CN 1914156 | A | 20070214 | CN 2005-80003641 | 20050126 |
| BR 2005006574 | A | 20070410 | BR 2005-6574 | 20050126 |
| JP 2007519666 | T | 20070719 | JP 2006-550082 | 20050126 |
| MX 2006PA08046 | A | 20061019 | MX 2006-PA8046 | 20060714 |
| KR 2007011283 | A | 20070124 | KR 2006-715350 | 20060728 |
| IN 2006CN03130 | A | 20070608 | IN 2006-CN3130 | 20060829 |

PRIORITY APPLN. INFO.: DE 2004-102004004672A 20040129
 WO 2005-EP725 W 20050126

OTHER SOURCE(S): CASREACT 143:195579

AB A method is described for the production of 3-pentenenitrile by the hydrocyanation of 1,3-butadiene in the presence of at least one catalyst, where the 1,3-butadiene which has not been hydrocyanated is removed from the product from the hydrocyanation reaction and recycled into the initial hydrocyanation process and the recycled 1,3-butadiene is monitored (e.g., liquid-phase IR spectroscopy) for hydrogen cyanide content.

IC ICM C07C253-10
 ICS C07C255-07

CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)
 Section cross-reference(s): 23, 48

ST pentenenitrile manuf catalytic hydrocyanation butadiene hydrogen cyanide process control

IT Alkadienes
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (1,3-butadiene; process control in a catalytic hydrocyanation method for the conversion of 1,3-butadiene and hydrogen cyanide into 3-pentenenitrile)

IT Phosphines
 Phosphites
 Phosphonates
 RL: CAT (Catalyst use); USES (Uses)
 (ligands; process control in a catalytic hydrocyanation method for the conversion of 1,3-butadiene and hydrogen cyanide into 3-pentenenitrile using)

IT Hydrocyanation
 Hydrocyanation catalysts
 Process control
 (process control in a catalytic hydrocyanation method for the conversion of 1,3-butadiene and hydrogen cyanide into 3-pentenenitrile)

IT Density
 Dielectric constant
 Gas chromatography
 Heat capacity
 IR spectroscopy
 (process control in a catalytic hydrocyanation method for the conversion of 1,3-butadiene and hydrogen cyanide into 3-pentenenitrile using)

IT Nitriles, preparation

RL: IMF (Industrial manufacture); PREP (Preparation)
 (unsatd., 3-pentenenitrile; process control in a catalytic hydrocyanation method for the conversion of 1,3-butadiene and hydrogen cyanide into 3-pentenenitrile)

IT 4635-87-4P, 3-Pentenenitrile
 RL: IMF (Industrial manufacture); PREP (Preparation)
 (process control in a catalytic hydrocyanation method for the conversion of 1,3-butadiene and hydrogen cyanide into 3-pentenenitrile)

IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,
 1,3-Butadiene, reactions
 RL: RCT (Reactant); PACT (Reactant or reagent)
 (process control in a catalytic hydrocyanation method for the conversion of 1,3-butadiene and hydrogen cyanide into 3-pentenenitrile)

IT 4635-87-4P, 3-Pentenenitrile
 RL: IMF (Industrial manufacture); PREP (Preparation)
 (process control in a catalytic hydrocyanation method for the conversion of 1,3-butadiene and hydrogen cyanide into 3-pentenenitrile)

RN 4635-87-4 CAPLUS
 CN 3-Pentenenitrile (CA INDEX NAME)



IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,
 1,3-Butadiene, reactions
 RL: RCT (Reactant); PACT (Reactant or reagent)
 (process control in a catalytic hydrocyanation method for the conversion of 1,3-butadiene and hydrogen cyanide into 3-pentenenitrile)

RN 74-90-8 CAPLUS
 CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 CAPLUS
 CN 1,3-Butadiene (CA INDEX NAME)



REFERENCE COUNT: 1 THERE ARE 1 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L88 ANSWER 7 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN DUPLICATE 7
 ACCESSION NUMBER: 2005:729615 CAPLUS Full-text
 DOCUMENT NUMBER: 143:195578
 TITLE: Catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of

INVENTOR(S): Jungkamp, Tim; Kunsmann-Keitel, Dagmar Pascale;
 Bartsch, Michael; Baumann, Robert; Haderlein, Gerd;
 Luyken, Hermann; Scheidel, Jens
 PATENT ASSIGNEE(S): BASF Aktiengesellschaft, Germany
 SOURCE: PCT Int. Appl., 24 pp.
 CODEN: PIXXD2
 DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|--|------|----------|-----------------------|------------|
| WO 2005073168 | A1 | 20050811 | WO 2005-EP723 | 20050126 |
| W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, RU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW | | | | |
| RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, RU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG | | | | |
| DE 102004004684 | A1 | 20050818 | DE 2004-102004004684 | 20040129 |
| CA 2560096 | A1 | 20050811 | CA 2005-2560096 | 20050126 |
| EP 1713761 | A1 | 20061025 | EP 2005-707006 | 20050126 |
| R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, FI, RO, CY, TR, BG, CZ, EE, HU, PL, SK, IS | | | | |
| CN 1914158 | A | 20070214 | CN 2005-80003677 | 20050126 |
| BR 2005007199 | A | 20070626 | BR 2005-7199 | 20050126 |
| JP 2007519664 | T | 20070719 | JP 2005-550080 | 20050126 |
| MX 2006PA07750 | A | 20060926 | MX 2006-PA7750 | 20060706 |
| US 2007155977 | A1 | 20070705 | US 2006-586490 | 20060720 |
| IN 2006CN03126 | A | 20070608 | IN 2006-CN3126 | 20060829 |
| PRIORITY APPLN. INFO.: | | | DE 2004-102004004684A | 20040129 |
| | | | WO 2005-EP723 | W 20050126 |

OTHER SOURCE(S): CASREACT 143:195578

AB A method for the production of 3-pentenenitrile is described which comprises the hydrocyanation of 1,3-butadiene with HCN over at least one catalyst, where the 1,3-butadiene and/or HCN is brought into contact with at least one microporous solid (e.g., 4A mol. sieves) prior to the reaction.

IC C07C253-10

CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)

Section cross-reference(s): 23, 48

ST catalytic hydrocyanation butadiene manuf pentenenitrile microporous solid usage

IT Alkadienes

RL: RCT (Reactant); RACT (Reactant or reagent)

(1,3-butadiene; catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenenitrile)

IT Hydrocyanation

Hydrocyanation catalysts

Molecular sieves

(catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenenitrile)

- IT Air
 (catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenenitrile using)
- IT Noble gases, uses
 RL: NUU (Other use, unclassified); USES (Uses)
 (gases; catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenenitrile using)
- IT Porous materials
 (microporous; catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenenitrile)
- IT Drying
 (of microporous solid; catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenenitrile)
- IT Nitriles, preparation
 RL: IMF (Industrial manufacture); PREP (Preparation)
 (unsatd., 3-pentenenitrile; catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenenitrile)
- IT 16529-56-9P, 2-Methyl-3-butenenitrile
 RL: BYP (Byproduct); PREP (Preparation)
 (catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenenitrile)
- IT 4635-87-4P, 3-Pentenenitrile
 RL: IMF (Industrial manufacture); PREP (Preparation)
 (catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenenitrile)
- IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,
 1,3-Butadiene, reactions
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenenitrile)
- IT 7727-37-9, Nitrogen, uses
 RL: NUU (Other use, unclassified); USES (Uses)
 (catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenenitrile using)
- IT 74-86-2, Acetylene, uses
 RL: NUU (Other use, unclassified); USES (Uses)
 (feed impurity; catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenenitrile)
- IT 1344-28-1, Alumina, processes
 RL: NUU (Other use, unclassified); PEP (Physical, engineering or chemical process); PYP (Physical process); PROC (Process); USES (Uses)
 (microporous solid; catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenenitrile)
- IT 4635-87-4P, 3-Pentenenitrile
 RL: IMF (Industrial manufacture); PREP (Preparation)
 (catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenenitrile)
- RN 4635-87-4 CAPLUS

10/586490

CN 3-Pentenenitrile (CA INDEX NAME)



IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,
1,3-Butadiene, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)
(catalytic hydrocyanation of 1,3-butadiene with hydrogen
cyanide in the presence of at least one microporous solid for
the manufacture of 3-pentenenitrile)

RN 74-90-8 CAPLUS

CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 CAPLUS

CN 1,3-Butadiene (CA INDEX NAME)



IT 7727-37-9, Nitrogen, uses

RL: NUU (Other use, unclassified); USES (Uses)
(catalytic hydrocyanation of 1,3-butadiene with hydrogen
cyanide in the presence of at least one microporous solid for
the manufacture of 3-pentenenitrile using)

RN 7727-37-9 CAPLUS

CN Nitrogen (CA INDEX NAME)



IT 1344-28-1, Alumina, processes

RL: NUU (Other use, unclassified); PEP (Physical, engineering or chemical
process); PYP (Physical process); PROC (Process); USES (Uses)
(microporous solid; catalytic hydrocyanation of
1,3-butadiene with hydrogen cyanide in the presence of at least one
microporous solid for the manufacture of 3-pentenenitrile)

RN 1344-28-1 CAPLUS

CN Aluminum oxide (Al₂O₃) (CA INDEX NAME)

*** STRUCTURE DIAGRAM IS NOT AVAILABLE ***

REFERENCE COUNT: 3 THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS
RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L88 ANSWER 8 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN DUPLICATE 8
 ACCESSION NUMBER: 2005:729614 CAPLUS Full-text
 DOCUMENT NUMBER: 143:195577
 TITLE: Method for the production of adiponitrile by the
 catalytic hydrocyanation of 1,3-butadiene
 INVENTOR(S): Bartsch, Michael; Baumann, Robert; Haderlein, Gerd;
 Flores, Miguel Angel; Jungkamp, Tim; Luyken, Hermann;
 Scheidel, Jens; Siegel, Wolfgang
 PATENT ASSIGNEE(S): BASF Aktiengesellschaft, Germany
 SOURCE: PCT Int. Appl., 49 pp.
 CODEN: PIXKD2
 DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|--|------|----------|-----------------------|------------|
| WO 2005073167 | A1 | 20050811 | WO 2005-EP717 | 20050126 |
| W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW | | | | |
| RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG | | | | |
| DE 102004004682 | A1 | 20050818 | DE 2004-102004004682 | 20040129 |
| CA 2553011 | A1 | 20050811 | CA 2005-2553011 | 20050126 |
| EP 1713759 | A1 | 20061025 | EP 2005-701177 | 20050126 |
| R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, FI, RO, CY, TR, BG, CZ, EE, HU, PL, SK, IS | | | | |
| CN 1914160 | A | 20070214 | CN 2005-80003694 | 20050126 |
| BR 2005007184 | A | 20070626 | BR 2005-7184 | 20050126 |
| JP 2007519663 | T | 20070719 | JP 2006-550078 | 20050126 |
| MX 2006PA07756 | A | 20060926 | MX 2006-PA7756 | 20060706 |
| KR 2007011279 | A | 20070124 | KR 2006-715317 | 20060728 |
| IN 2006CN03131 | A | 20070727 | IN 2006-CN3131 | 20060829 |
| PRIORITY APPLN. INFO.: | | | DE 2004-102004004682A | 20040129 |
| | | | WO 2005-EP717 | W 20050126 |

OTHER SOURCE(S): CASREACT 143:195577

AB A method for the production of adiponitrile by hydrocyanation of 1,3-butadiene over a catalyst is described where, in a first step, 1,3-butadiene is hydrocyanated into 3-pentenenitrile over at least one elemental nickel catalyst and, in a second step, the 3-pentenenitrile intermediate is hydrocyanated to form adiponitrile over an elemental nickel catalyst with the addition of at least one Lewis acid. At least one of the elemental nickel catalysts used in the resp. steps is converted in the other step. Process flow diagrams are presented.

IC ICM C07C253-10

ICS C07C253-30

CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)

Section cross-reference(s): 23, 48, 67

ST adiponitrile manuf butadiene catalytic hydrocyanation

IT Alkadienes

RL: EPR (Engineering process); PEP (Physical, engineering or chemical

- process); RCT (Reactant); PROC (Process); RACT (Reactant or reagent)
 (1,3-butadiene; method for the production of adiponitrile by the
 catalytic hydrocyanation of 1,3-butadiene using)
- IT Nitriles, preparation
 RL: EPR (Engineering process); IMF (Industrial manufacture); PEP
 (Physical, engineering or chemical process); PREP (Preparation); PROC
 (Process)
 (dinitriles, adiponitrile; method for the production of adiponitrile by the
 catalytic hydrocyanation of 1,3-butadiene)
- IT Hydrocyanation catalysts
 (elemental nickel complexes; method for the production of adiponitrile by
 the catalytic hydrocyanation of 1,3-butadiene)
- IT Hydrocyanation
 (method for the production of adiponitrile by the catalytic
 hydrocyanation of 1,3-butadiene)
- IT Distillation
 Distillation columns
 Extraction
 Isomerization
 (method for the production of adiponitrile by the catalytic
 hydrocyanation of 1,3-butadiene using)
- IT Lewis acids
 RL: CAT (Catalyst use); EPR (Engineering process); PEP (Physical,
 engineering or chemical process); PROC (Process); USES (Uses)
 (method for the production of adiponitrile by the catalytic
 hydrocyanation of 1,3-butadiene using)
- IT 111-69-3P, Adiponitrile
 RL: EPR (Engineering process); IMF (Industrial manufacture); PEP
 (Physical, engineering or chemical process); PREP (Preparation); PROC
 (Process)
 (method for the production of adiponitrile by the catalytic
 hydrocyanation of 1,3-butadiene)
- IT 4635-87-8P, 3-Pentenenitrile 13284-42-9P, 2-Pentenenitrile
 RL: EPR (Engineering process); IMF (Industrial manufacture); PEP
 (Physical, engineering or chemical process); RCT (Reactant); PREP
 (Preparation); PROC (Process); RACT (Reactant or reagent)
 (method for the production of adiponitrile by the catalytic
 hydrocyanation of 1,3-butadiene)
- IT 106-99-0, 1,3-Butadiene, reactions
 RL: EPR (Engineering process); PEP (Physical, engineering or chemical
 process); RCT (Reactant); PROC (Process); RACT (Reactant or
 reagent)
 (method for the production of adiponitrile by the catalytic
 hydrocyanation of 1,3-butadiene)
- IT 7646-85-7, Zinc chloride, processes 7718-54-9, Nickel chloride,
 processes
 RL: CAT (Catalyst use); EPR (Engineering process); PEP (Physical,
 engineering or chemical process); PROC (Process); USES (Uses)
 (method for the production of adiponitrile by the catalytic
 hydrocyanation of 1,3-butadiene using)
- IT 4403-61-6P, 2-Methyl-2-butenenitrile 16529-56-9P, 2-Methyl-3-
 butenenitrile 28906-50-5P, Methylglutaronitrile
 RL: EPR (Engineering process); IMF (Industrial manufacture); PEP
 (Physical, engineering or chemical process); RCT (Reactant); PREP
 (Preparation); PROC (Process); RACT (Reactant or reagent)
 (method for the production of adiponitrile by the catalytic
 hydrocyanation of 1,3-butadiene using)
- IT 74-90-8, Hydrogen cyanide, reactions
 RL: EPR (Engineering process); PEP (Physical, engineering or chemical
 process); RCT (Reactant); PROC (Process); RACT (Reactant or

reagent)

(method for the production of adiponitrile by the catalytic hydrocyanation of 1,3-butadiene using)

IT 4635-87-4P, 3-Pentenenitrile

RL: EPR (Engineering process); IMF (Industrial manufacture); PEP (Physical, engineering or chemical process); RCT (Reactant); PREP (Preparation); PROC (Process); RACT (Reactant or reagent)

(method for the production of adiponitrile by the catalytic hydrocyanation of 1,3-butadiene)

RN 4635-87-4 CAPLUS

CN 3-Pentenenitrile (CA INDEX NAME)



IT 106-99-0, 1,3-Butadiene, reactions

RL: EPR (Engineering process); PEP (Physical, engineering or chemical process); RCT (Reactant); PROC (Process); RACT (Reactant or reagent)

(method for the production of adiponitrile by the catalytic hydrocyanation of 1,3-butadiene)

RN 106-99-0 CAPLUS

CN 1,3-Butadiene (CA INDEX NAME)



IT 74-90-8, Hydrogen cyanide, reactions

RL: EPR (Engineering process); PEP (Physical, engineering or chemical process); RCT (Reactant); PROC (Process); RACT (Reactant or reagent)

(method for the production of adiponitrile by the catalytic hydrocyanation of 1,3-butadiene using)

RN 74-90-8 CAPLUS

CN Hydrocyanic acid (CA INDEX NAME)



REFERENCE COUNT: 13 THERE ARE 13 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L88 ANSWER 9 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN DUPLICATE 9

ACCESSION NUMBER: 2005:729613 CAPLUS Full-text

DOCUMENT NUMBER: 143:195576

TITLE: Catalytic hydrocyanation method for the production of pentenenitriles from 1,3-butadiene and hydrogen cyanide

INVENTOR(S): Bartsch, Michael; Baumann, Robert; Haderlein, Gerd;

Schindler, Goetz-Peter; Jungkamp, Tim; Luyken,
Hermann; Scheidel, Jens; Brodhagen, Andreas
PATENT ASSIGNEE(S): BASF Aktiengesellschaft, Germany

SOURCE: PCT Int. Appl., 31 pp.
CODEN: PIXXD2

DOCUMENT TYPE:

Patent
LANGUAGE:

German
FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|--|------|----------|-----------------------|------------|
| WO 2005073166 | A2 | 20050811 | WO 2005-EP773 | 20050127 |
| WO 2005073166 | A3 | 20070301 | | |
| W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, US, UZ, VC, VN, YU, ZA, ZM, ZW, SM RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG | | | | |
| DE 102004004697 | A1 | 20050818 | DE 2004-102004004697 | 20040129 |
| EP 1716102 | A2 | 20061102 | EP 2005-701202 | 20050127 |
| R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, HU, PL, SK, BA, HR, IS, YU | | | | |
| CN 1997624 | A | 20070711 | CN 2005-80003692 | 20050127 |
| JP 2007522122 | T | 20070809 | JP 2006-550096 | 20050127 |
| PRIORITY APPLN. INFO.: | | | DE 2004-102004004697A | 20040129 |
| | | | WO 2005-EP773 | W 20050127 |

OTHER SOURCE(S): CASREACT 143:195576

- AB A method is described for the hydrocyanation of 1,3-butadiene into pentenenitriles using at least one elemental Ni complex with phosphorous-containing ligands as a catalyst, where the 1,3-butadiene is used in a mixture with butane and the mixture contains 60-90 volume% 1,3-butadiene and 10-40 volume% butane.
- IC ICM C07C253-00
- CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)
Section cross-reference(s): 23, 67
- ST pentenenitrile manuf catalytic hydrocyanation butadiene
- IT Hydrocyanation catalysts
(catalytic hydrocyanation method for the production of pentenenitriles from 1,3-butadiene and hydrogen cyanide)
- IT Hydrocyanation catalysts
(elemental Ni complexes and P-containing ligands; catalytic hydrocyanation method for the production of pentenenitriles from 1,3-butadiene and hydrogen cyanide)
- IT Petroleum products
(gases, liquefied; in a catalytic hydrocyanation method for the production of pentenenitriles from 1,3-butadiene and hydrogen cyanide)
- IT Phosphines
- Phosphites
- RL: CAT (Catalyst use); USES (Uses)
(ligands; in a catalytic hydrocyanation method for the production of pentenenitriles from 1,3-butadiene and hydrogen cyanide)
- IT Nitriles, preparation

RL: IMF (Industrial manufacture); PREP (Preparation)
 (unsatd., pentenenitriles; catalytic hydrocyanation method
 for the production of pentenenitriles from 1,3-butadiene and hydrogen
 cyanide)

IT 1295-35-8 509083-87-8
 RL: CAT (Catalyst use); USES (Uses)
 (catalytic hydrocyanation method for the production of
 pentenenitriles from 1,3-butadiene and hydrogen cyanide)

IT 4635-87-4P, 3-Pentenenitrile 16529-56-9P, 2-Methyl-3-
 butenenitrile
 RL: IMF (Industrial manufacture); PREP (Preparation)
 (catalytic hydrocyanation method for the production of
 pentenenitriles from 1,3-butadiene and hydrogen cyanide)

IT 106-97-8, Butane, reactions
 RL: NUU (Other use, unclassified); RCT (Reactant); RACT (Reactant or
 reagent); USES (Uses)
 (catalytic hydrocyanation method for the production of
 pentenenitriles from 1,3-butadiene and hydrogen cyanide)

IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,
 1,3-Butadiene, reactions
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (catalytic hydrocyanation method for the production of
 pentenenitriles from 1,3-butadiene and hydrogen cyanide)

IT 4635-87-4P, 3-Pentenenitrile
 RL: IMF (Industrial manufacture); PREP (Preparation)
 (catalytic hydrocyanation method for the production of
 pentenenitriles from 1,3-butadiene and hydrogen cyanide)

RN 4635-87-4 CAPLUS
 CN 3-Pentenenitrile (CA INDEX NAME)



IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,
 1,3-Butadiene, reactions
 RL: RCT (Reactant); PACT (Reactant or reagent)
 (catalytic hydrocyanation method for the production of
 pentenenitriles from 1,3-butadiene and hydrogen cyanide)

RN 74-90-8 CAPLUS
 CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 CAPLUS
 CN 1,3-Butadiene (CA INDEX NAME)



L88 ANSWER 10 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN DUPLICATE 10
 ACCESSION NUMBER: 2003:319912 CAPLUS Full-text
 DOCUMENT NUMBER: 138:321395
 TITLE: Phosphonites, use thereof as ligand in transition metal complexes and method for production of nitriles
 INVENTOR(S): Bartsch, Michael; Baumann, Robert; Kunsmann-Keitel, Dagmar Pascale; Haderlein, Gerd; Jungkamp, Tim; Altmaier, Marco; Siegel, Wolfgang; Molnar, Ferenc
 PATENT ASSIGNEE(S): BASF Aktiengesellschaft, Germany
 SOURCE: PCT Int. Appl., 32 pp.
 CODEN: PIXXD2
 DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|---|--|------------------|------------------|----------|
| WO 2003033509 | A1 | 20030424 | WO 2002-EP11107 | 20021004 |
| W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW | | | | |
| RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG | | | | |
| DE 10150281 | A1 | 20030430 | DE 2001-10150281 | 20011012 |
| DE 10207165 | A1 | 20030821 | DE 2002-10207165 | 20020220 |
| CA 2464710 | A1 | 20030424 | CA 2002-2464710 | 20021004 |
| AU 2002362815 | A1 | 20030428 | AU 2002-362815 | 20021004 |
| EP 1438317 | A1 | 20040721 | EP 2002-801308 | 20021004 |
| EP 1438317 | B1 | 20060621 | | |
| R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, SK | | | | |
| BR 2002012965 | A | 20041013 | BR 2002-12965 | 20021004 |
| JP 2005505630 | T | 20050224 | JP 2003-536248 | 20021004 |
| CN 1639176 | A | 20050713 | CN 2002-819907 | 20021004 |
| AT 330962 | T | 20060715 | AT 2002-801308 | 20021004 |
| ES 2266630 | T3 | 20070301 | ES 2002-2801308 | 20021004 |
| MX 2004PA02139 | A | 20040629 | MX 2004-PA2139 | 20040305 |
| US 2005090678 | A1 | 20050428 | US 2004-491918 | 20040408 |
| US 7067685 | B2 | 20060627 | | |
| IN 2004CN01004 | A | 20060203 | IN 2004-CN1004 | 20040511 |
| PRIORITY APPLN. INFO.: | | | | |
| | | DE 2001-10150281 | A | 20011012 |
| | | DE 2002-10207165 | A | 20020220 |
| | | WO 2002-EP11107 | W | 20021004 |
| OTHER SOURCE(S): GI | CASREACT 138:321395; MARPAT 138:321395 | | | |

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

- AB The invention relates to phosphinites I and II (R₁, R₂, R₅, R₆, R₇, R₈, R₉ = independently represent H, Cl-8 alkyl or alkylene, or Cl-8 alkoxy; R₃ = H, Me; R₄ = i-Pr, t-butyl; X = F, Cl or CF₃; n = 1, 2) useful as cocatalysts for nickel catalyzed preparation of nitriles. Thus, nickel(0)/phosphonite-catalyzed isomerization of 2-methyl-3- butenenitrile to give 3-pentenenitrile and same catalyst mediated hydrocyanation of 3-pentenenitrile to give adipodinitrile is described.
- IC ICM C07F009-48
ICS C07C253-10; B01J031-18
CC 29-7 (Organometallic and Organometalloidal Compounds)
Section cross-reference(s): 23, 67
ST phosphonite nickel catalyzed isomerization hydrocyanation; nitrile dinitrile prepn
IT Hydrocyanation catalysts
Isomerization catalysts
(use of phosphonites as cocatalysts in nickel complex catalyzed production of nitriles)
IT Nitriles, preparation
RL: SPN (Synthetic preparation); PREP (Preparation)
(use of phosphonites as cocatalysts in nickel complex catalyzed production of nitriles)
IT 7646-85-7, Zinc dichloride, uses
RL: CAT (Catalyst use); USES (Uses)
(additive; use of phosphonites as cocatalysts in nickel complex catalyzed production of nitriles)
IT 106-99-0, 1,3-Butadiene, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(hydrocyanation; use of phosphonites as cocatalysts in nickel complex catalyzed production of nitriles)
IT 4635-87-4P, 3-Pentenenitrile
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(hydrocyanation; use of phosphonites as cocatalysts in nickel complex catalyzed production of nitriles)
IT 16529-56-9, 2-Methyl-3-butenenitrile
RL: RCT (Reactant); RACT (Reactant or reagent)
(isomerization; use of phosphonites as cocatalysts in nickel complex catalyzed production of nitriles)
IT 592-18-8P, 4-Pentenenitrile 16529-66-1P, trans-3-Pentenenitrile 16545-78-1P, cis-3-Pentenenitrile 20068-02-4P, cis-2-Methyl-2-butenenitrile 26294-98-4P, trans-2-Pentenenitrile 28906-50-5P, Methylglutaronitrile 30574-97-1P, trans-2-Methyl-2-butenenitrile
RL: BYP (Byproduct); PREP (Preparation)
(use of phosphonites as cocatalysts in nickel complex catalyzed production of nitriles)
IT 1295-35-8, Bis(1,5-cyclooctadiene)nickel 125280-25-3 494227-34-8
512172-91-7 512172-92-8 512172-93-9 512172-94-0 512172-95-1
RL: CAT (Catalyst use); USES (Uses)
(use of phosphonites as cocatalysts in nickel complex catalyzed production of nitriles)
IT 74-90-3, Hydrogen cyanide, reactions
RL: FCT (Reactant); PACT (Reactant or reagent)
(use of phosphonites as cocatalysts in nickel complex catalyzed production of nitriles)
IT 111-69-3P, Adipodinitrile
RL: SPN (Synthetic preparation); PREP (Preparation)
(use of phosphonites as cocatalysts in nickel complex catalyzed production of nitriles)
IT 106-99-0, 1,3-Butadiene, reactions

10/586490

RL: RCT (Reactant); RACT (Reactant or reagent)
(hydrocyanation; use of phosphonites as cocatalysts in nickel
complex catalyzed production of nitriles)
RN 106-99-0 CAPLUS
CN 1,3-Butadiene (CA INDEX NAME)

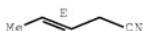


IT 4635-87-4E, 3-Pentenenitrile
RL: RCT (Reactant); SPN (Synthetic preparation); PREP
(Preparation); RACT (Reactant or reagent)
(hydrocyanation; use of phosphonites as cocatalysts in nickel
complex catalyzed production of nitriles)
RN 4635-87-4 CAPLUS
CN 3-Pentenenitrile (CA INDEX NAME)



IT 16529-66-1P, trans-3-Pentenenitrile 16545-78-1P,
cis-3-Pentenenitrile
RL: BYP (Byproduct); PREP (Preparation)
(use of phosphonites as cocatalysts in nickel complex
catalyzed production of nitriles)
RN 16529-66-1 CAPLUS
CN 3-Pentenenitrile, (3E)- (CA INDEX NAME)

Double bond geometry as shown.



RN 16545-78-1 CAPLUS
CN 3-Pentenenitrile, (3Z)- (CA INDEX NAME)

Double bond geometry as shown.



IT 74-90-8, Hydrogen cyanide, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(use of phosphonites as cocatalysts in nickel complex
catalyzed production of nitriles)
RN 74-90-8 CAPLUS
CN Hydrocyanic acid (CA INDEX NAME)

N
CH

REFERENCE COUNT: 2 THERE ARE 2 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L88 ANSWER 11 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN DUPLICATE 11
 ACCESSION NUMBER: 1995:854364 CAPLUS Full-text
 DOCUMENT NUMBER: 124:55389
 TITLE: Vapor phase hydrocyanation of diolefinic compounds catalyzed by nickel complexes with bidentate phosphite ligands
 INVENTOR(S): Druliner, Joe D.
 PATENT ASSIGNEE(S): E. I. Du Pont de Nemours & Co., USA
 SOURCE: U.S., 7 pp.
 CODEN: USXXAM
 DOCUMENT TYPE: Patent
 LANGUAGE: English
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|--|--------------------------------------|----------|-----------------|------------|
| US 5449807 | A | 19950912 | US 1994-342195 | 19941118 |
| CA 2200700 | A1 | 19960530 | CA 1995-2200700 | 19951101 |
| CA 2200700 | C | 20070109 | | |
| WO 9616022 | A1 | 19960530 | WO 1995-US14787 | 19951101 |
| W: BR, CA, CN, JP, KR, SG | | | | |
| RW: AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE | | | | |
| EP 792259 | A1 | 19970903 | EP 1995-941390 | 19951101 |
| EP 792259 | B1 | 19990804 | | |
| R: AT, BE, CH, DE, ES, FR, GB, IT, LI, NL, SE | | | | |
| CN 1163606 | A | 19971029 | CN 1995-196276 | 19951101 |
| CN 1068307 | B | 20010711 | | |
| BR 9510347 | A | 19971223 | BR 1995-10347 | 19951101 |
| JP 10509954 | T | 19980929 | JP 1995-516952 | 19951101 |
| AT 182881 | T | 19990815 | AT 1995-941390 | 19951101 |
| ES 2138761 | T3 | 20000116 | ES 1995-941390 | 19951101 |
| JP 3476399 | B2 | 20031215 | JP 1996-516952 | 19951101 |
| PRIORITY APPLN. INFO.: | | | US 1994-342195 | A 19941118 |
| | | | WO 1995-US14787 | W 19951101 |
| OTHER SOURCE(S): | CASREACT 124:55389; MARPAT 124:55389 | | | |
| GI | | | | |

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

AB A process is claimed for the gas-phase hydrocyanation of diolefinic compds. comprising, reacting an acyclic, aliphatic, conjugated diolefinic compound with HCN in the gas phase within a temperature range of 135-170° in the presence of a supported catalyst composition comprising zero-valent nickel and at least one bidentate phosphite ligand selected from the group represented by I wherein each R₁, independently, is a secondary or tertiary hydrocarbyl of 3

to 12 carbon atoms; each R2, independently, is H, a C1 to C12 alkyl, or OR3, wherein R3 is C1 to C12 alkyl; and II wherein each R4, independently, is a tertiary hydrocarbon of up to 12 carbon atoms, or OR5, wherein R5 is a C1 to C12 alkyl; and each R6, independently, is a tertiary hydrocarbon of up to 12 carbon atoms, to produce acyclic olefinic nitriles in which the olefinic double bond is not conjugated with the cyano group. Thus, e.g., hydrocyanation of 1,3-butadiene catalyzed by silica-supported Ni(0)LCH₂:CH₂ with L = II (R4 = OMe, R6 = tert-Bu) (preparation given) resulted, after 1,5 h, in 76.4% conversion of BD and 90.4% conversion to pentenenitriles [3- + 4-pentenenitrile + 2-methyl-3-butenenitrile]; no pentenenitrile products were observed when a zinc copper chromite catalyst was used.

IC ICM C07C253-10

INCL 558338000

CC 23-19 (Aliphatic Compounds)

Section cross-reference(s): 35

ST pentenenitrile; butadiene hydrocyanation nickel bidentate phosphite catalyst

IT Hydrocyanation catalysts

(vapor phase hydrocyanation of butadiene catalyzed by nickel complexes with bidentate phosphite ligands)

IT 1344-28-1, Alumina, uses 7440-44-0, Carbon, uses 7631-86-9, Silica, uses

RL: CAT (Catalyst use); USES (Uses)
(catalyst support; vapor phase hydrocyanation of butadiene catalyzed by nickel complexes with bidentate phosphite ligands)

IT 169254-14-2P

RL: BYP (Byproduct); PREP (Preparation)
(vapor phase hydrocyanation of butadiene catalyzed by nickel complexes with bidentate phosphite ligands)

IT 169254-15-3P

RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);
USES (Uses)
(vapor phase hydrocyanation of butadiene catalyzed by nickel complexes with bidentate phosphite ligands)

IT 592-51-8P, 4-Pentenenitrile 4635-87-4P, 3-Pentenenitrile

16529-56-9P, 2-Methyl-3-butenenitrile

RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PPEP
(Preparation)
(vapor phase hydrocyanation of butadiene catalyzed by nickel complexes with bidentate phosphite ligands)

IT 74-85-1, Ethene, reactions 74-96-2, Hydrogen cyanide, reactions 106-99-0, 1,3-Butadiene, reactions 121627-17-6

RL: PCT (Reactant); FACT (Reactant or reagent)
(vapor phase hydrocyanation of butadiene catalyzed by nickel complexes with bidentate phosphite ligands)

IT 1344-28-1, Alumina, uses

RL: CAT (Catalyst use); USES (Uses)
(catalyst support; vapor phase hydrocyanation of butadiene catalyzed by nickel complexes with bidentate phosphite ligands)

RN 1344-28-1 CAPLUS

CN Aluminum oxide (Al2O3) (CA INDEX NAME)

*** STRUCTURE DIAGRAM IS NOT AVAILABLE ***

IT 4635-87-4P, 3-Pentenenitrile

RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP
(Preparation)
(vapor phase hydrocyanation of butadiene catalyzed by nickel complexes with bidentate phosphite ligands)

RN 4635-87-4 CAPLUS

CN 3-Pentenenitrile (CA INDEX NAME)



IT 74-90-3, Hydrogen cyanide, reactions 106-99-0,
 1,3-Butadiene, reactions
 RL: PCT (Reactant); FACT (Reactant or reagent;
 (vapor phase hydrocyanation of butadiene catalyzed by nickel
 complexes with bidentate phosphite ligands)
 RN 74-90-8 CAPLUS
 CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 CAPLUS
 CN 1,3-Butadiene (CA INDEX NAME)



L88 ANSWER 12 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN DUPLICATE 12
 ACCESSION NUMBER: 1988:131003 CAPLUS Full-text
 DOCUMENT NUMBER: 108:131003
 TITLE: The stereochemistry of organometallic compounds.
 XXVIII. The nickel-catalyzed addition of hydrogen
 cyanide to aliphatic dienes
 AUTHOR(S): Campi, Eva M.; Elmes, Patricia S.; Jackson, W. Roy;
 Lovel, Craig G.; Probert, Michael K. S.
 CORPORATE SOURCE: Dep. Chem., Monash Univ., Clayton, 3168, Australia
 SOURCE: Australian Journal of Chemistry (1987), 40(6), 1053-61
 CODEN: AJCHAS; ISSN: 0004-9425
 DOCUMENT TYPE: Journal
 LANGUAGE: English
 OTHER SOURCE(S): CASREACT 108:131003
 AB Hydrocyanation of a variety of aliphatic dienes, e.g. ($\text{H}_2\text{C}:\text{CH}_2$) 2CH_2 , in the
 presence of Ni(O) complexes gave diene rearrangement products and β,γ -unsatd.
 nitriles, e.g. MeCH:CHCHMeCn, in 10-90% yields. The use of chiral Ni complexes
 gave only low levels of asym. induction. A mechanism involving π -allyl Ni
 intermediates is proposed.
 CC 23-19 (Aliphatic Compounds)
 ST diene hydrocyanation nickel catalyst; nitrile unsatd; regiochem diene
 hydrocyanation mechanism
 IT Hydrocyanation catalysts
 (nickel complexes, for dienes to unsatd. nitriles)
 IT 84786-32-3 113065-29-5
 RL: CAT (Catalyst use); USES (Uses)
 (catalyst, for hydrocyanation of dienes)

10/586490

IT 14221-00-2

RL: CAT (Catalyst use); USES (Uses)
(catalysts, for hydrocyanation of butadiene and pentadiene)

IT 101-02-0, Triphenylphosphite 32305-98-9 62144-65-4

RL: RCT (Reactant); RACT (Reactant or reagent)
(co-catalyst, for hydrocyanation of dienes)

IT 74-90-8, Hydrogen cyanide, reactions 75-86-5, Acetone
cyanohydrin 3017-23-0, Deuterium cyanide

RL: RCI (Reactant); RACT (Reactant or reagent)
(hydrocyanation by, of dienes, in the presence of nickel complexes)

IT 106-99-0, Buta-1,3-diene, reactions 591-93-5, Penta-1,4-diene
592-42-7, Hexa-1,5-diene 1647-16-1 3710-30-3, Octa-1,7-diene
5194-51-4 7319-00-8

RL: RCT (Reactant); RACT (Reactant or reagent)
(hydrocyanation of, in the presence of nickel complexes)

IT 74-90-8

RL: RCT (Reactant); RACT (Reactant or reagent)
(hydrocyanation, of dienes, unsatd. nitriles by)

IT 816-16-0P, Methyl 2-ethylpentanoate 816-63-7P 2177-81-3P, Methyl
2-methylhexanoate 2177-86-8P, Methyl 2-methyloctanoate 5162-60-7P
7732-18-5P, Water, preparation 16529-56-9P, 2-Methylbut-3-enenitrile
16529-66-1P 74669-69-5P 80651-37-2P

RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)

IT 74-90-8, Hydrogen cyanide, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)
(hydrocyanation by, of dienes, in the presence of nickel complexes)

RN 74-90-8 CAPLUS

CN Hydrocyanic acid (CA INDEX NAME)



IT 106-99-0, Buta-1,3-diene, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)
(hydrocyanation of, in the presence of nickel complexes)

RN 106-99-0 CAPLUS

CN 1,3-Butadiene (CA INDEX NAME)



IT 74-90-8

RL: RCT (Reactant); RACT (Reactant or reagent)
(hydrocyanation, of dienes, unsatd. nitriles by)

RN 74-90-8 CAPLUS

CN Hydrocyanic acid (CA INDEX NAME)



IT 16529-66-1P
 RL: SPN (Synthetic preparation); PFP (Preparation)
 (preparation of)
 RN 16529-66-1 CAPLUS
 CN 3-Pentenenitrile, (3E)- (CA INDEX NAME)

Double bond geometry as shown.



L88 ANSWER 13 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN
 ACCESSION NUMBER: 2005:729626 CAPLUS Full-text
 DOCUMENT NUMBER: 143:195589
 TITLE: Vacuum distillation method for the separation of pentenenitrile isomers
 INVENTOR(S): Jungkamp, Tim; Baumann, Robert; Bartsch, Michael; Haderlein, Gerd; Luyken, Hermann; Scheidel, Jens
 PATENT ASSIGNEE(S): BASF Aktiengesellschaft, Germany
 SOURCE: PCT Int. Appl., 33 pp.
 CODEN: PIXXD2
 DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|--|------|----------|--|------------------------|
| WO 2005073179 | A1 | 20050811 | WO 2005-EP726 | 20050126 |
| W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JE, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, US, UZ, VC, VN, YU, ZA, ZM, ZW RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG | | | | |
| DE 102004004721 | A1 | 20050818 | DE 2004-102004004721 | 20040129 |
| CA 2553776 | A1 | 20050811 | CA 2005-2553776 | 20050126 |
| EP 1713766 | A1 | 20061025 | EP 2005-707007 | 20050126 |
| R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, FI, RO, CY, TR, BG, CZ, EE, HU, PL, SK, IS | | | | |
| CN 1914167 | A | 20070214 | CN 2005-80003676 | 20050126 |
| BR 2005007196 | A | 20070626 | BR 2005-7196 | 20050126 |
| JP 2007519667 | T | 20070719 | JP 2006-550083 | 20050126 |
| MX 2006PA07754 | A | 20060926 | MX 2006-PA7754 | 20060706 |
| US 2007112215 | A1 | 20070517 | US 2006-586452 | 20060718 |
| IN 2006CN03127 | A | 20070608 | IN 2006-CN3127 | 20060829 |
| PRIORITY APPLN. INFO.: | | | DE 2004-102004004721A WO 2005-EP726 | 20040129 W 20050126 |

AB A vacuum distillation method for the separation of material mixts. of pentenenitrile isomers, prepared by the catalytic hydrocyanation of 1,3-butadiene with HCN, is described where at least one isomer of the mixture (e.g., 3-pentenenitrile) is enriched and the separation of the mixture of pentenenitrile mixts. is carried out by distillation at reduced pressures.

IC ICM C07C253-34
ICS C07C255-07

CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)
Section cross-reference(s): 23, 48

IT Hydrocyanation catalysts
(hydrocyanation of 1,3-butadiene into pentenenitrile isomers using)

IT 4635-87-4P, 3-Pentenenitrile 16529-56-9P, 2-Methyl-3-butenenitrile 16529-66-1P, trans-3-Pentenenitrile 16545-78-1P, cis-3-Pentenenitrile 20068-02-4P, cis-2-Methyl-2-butenenitrile 25899-50-7P, cis-2-Pentenenitrile 27236-41-5P, Pentenenitrile 30574-97-1P, trans-2-Methyl-2-butenenitrile

RL: PEP (Physical, engineering or chemical process); PNU (Preparation, unclassified); PUR (Purification or recovery); PYP (Physical process); PREP (Preparation); PROC (Process)
(vacuum distillation method for the separation of pentenenitrile isomers)

IT 74-90-3, Hydrogen cyanide, reactions 106-99-0,
1,3-Butadiene, reactions
RL: RCT (Reactant); RFACT (Reactant or reagent)
(vacuum distillation method for the separation of pentenenitrile isomers prepared from)

IT 4635-87-4P, 3-Pentenenitrile 16529-66-1P, trans-3-Pentenenitrile 16545-78-1P, cis-3-Pentenenitrile
RL: PEP (Physical, engineering or chemical process); PNU (Preparation, unclassified); PUR (Purification or recovery); PYP (Physical process); PREP (Preparation); PROC (Process)
(vacuum distillation method for the separation of pentenenitrile isomers)

RN 4635-87-4 CAPLUS
CN 3-Pentenenitrile (CA INDEX NAME)



RN 16529-66-1 CAPLUS
CN 3-Pentenenitrile, (3E)- (CA INDEX NAME)

Double bond geometry as shown.



RN 16545-78-1 CAPLUS
CN 3-Pentenenitrile, (3Z)- (CA INDEX NAME)

Double bond geometry as shown.



IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,
 1,3-Butadiene, reactions
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (vacuum distillation method for the separation of pentenenitrile isomers
 prepared
 from)
 RN 74-90-8 CAPLUS
 CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 CAPLUS
 CN 1,3-Butadiene (CA INDEX NAME)



REFERENCE COUNT: 2 THERE ARE 2 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L88 ANSWER 14 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN
 ACCESSION NUMBER: 2005:729625 CAPLUS Full-text
 DOCUMENT NUMBER: 143:195588
 TITLE: Recovery of hydrogen cyanide from 1,3-butadiene
 catalytic hydrocyanation reaction mixtures in the
 manufacture of 3-pentenenitriles by azeotropic
 distillation
 INVENTOR(S): Jungkamp, Tim; Polka, Hans-Martin; Baumann, Robert;
 Bartsch, Michael; Haderlein, Gerd; Luyken, Hermann;
 Scheidel, Jens
 PATENT ASSIGNEE(S): BASF Aktiengesellschaft, Germany
 SOURCE: PCT Int. Appl., 24 pp.
 CODEN: PIXXD2
 DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|---------------|---|----------|-----------------|----------|
| WO 2005073178 | A2 | 20050811 | WO 2005-EP724 | 20050126 |
| WO 2005073178 | A3 | 20050922 | | |
| W: | AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, | | | |

DE 102004004718 A1 20050818 DE 2004-102004004718 20040129
CA 2553766 A1 20050811 CA 2005-2553766 20050126

EP 1716109 A2 20061102 EP 2005-715209 20050126

R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT,

IE, SI, LT, FI, RO, CY, TR, BG, CZ, EE, HU, PL, SK, IS
CN 1914166 A 20070214 CN 2005-80003623 20050126

BR 2005007194 A 20070626 BR 2005-7194 20050126

JP 2007519665 T 20070719 JP 2006-550081 20050126

MX 2006PA07887 A 20061002 MX 2006-PA7887 20060710

IN 2006CN03124 A 20070608 IN 2006-CN3124 20060829

DE 2004-102004004718A 20040129
NO 0005 75501 -- 00050000

PRIORITY APPLN. INFO.: DE 2004-102004004718A 20040129
WO 2005-EP724 W 20050126

OTHER SOURCE(S): CASREACT 143:195588
AB A method is described for separating hydrogen cyanide from mixts. containing 3-pentenenitrile by means of the azeotropic distillation of hydrogen cyanide with 1,3-butadiene.

IC ICM C07C253-34
TCS C07C255-04; C07C255-07

CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)

Section cross-reference(s): 23, 48
IT Hydrocyanation catalysts

(Ni-P complexes; recovery of hydrogen cyanide from 1,3-butadiene catalytic hydrocyanation reaction mixts. in the manufacture of 3-pentenenitriles by azeotropic distillation)

IT Distillation
(azeotropic; recovery of hydrogen cyanide from 1,3-butadiene catalytic hydrocyanation reaction mixts. in the manufacture of 3-pentenonitriles by azeotropic distillation)

IT Hydrocyanation
(recovery of hydrogen cyanide from 1,3-butadiene catalytic hydrocyanation reaction mixts. in the manufacture of 3-pentenenitriles by azeotropic distillation)

IT Nitriles, preparation

RL: PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PYP (Physical process); PREP (Preparation); PROC (Process) (unsatd., 3-pentenenitriles; recovery of hydrogen cyanide from 1,3-butadiene catalytic hydrocyanation reaction mixts. in the manufacture of 3-pentenenitriles by azeotropic distillation)

IT 106-99-0P, 1,3-Butadiene, preparation
RL: NNU (Other use, unclassified); PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PYP (Physical process); RCT (Reactant); PREP (Preparation); PROC (Process); RACT (Reactant)

or reagent); USES (Uses) (azeotropic distillation agent; recovery of hydrogen cyanide from 1,3-butadiene catalytic hydrocyanation reaction mixts. in the manufacture of 3-pentenenitriles by azeotropic distillation)

IT 509083-87-8
BL: CAT (Catalyst use); USES (Uses)

RL: CAI (catalyst use); USES (Uses)
(ligand; recovery of hydrogen cyanide from 1,3-butadiene
catalytic hydrocyanation reaction mixts. in the manufacture of
3-nitrocaprolides by azeotropic distillation).

3-pentenenitriles by azeotropic distillation)

RL: CAT (Catalyst use); USES (Uses)
 (recovery of hydrogen cyanide from 1,3-butadiene catalytic
 hydrocyanation reaction mixts. in the manufacture of 3-pentenenitriles by
 azeotropic distillation)

IT 16529-66-1P, trans-3-Pentenenitrile 27236-41-5P, Pentenenitrile
 RL: IMF (Industrial manufacture); PEP (Physical, engineering or chemical
 process); PUR (Purification or recovery); PYP (Physical process);
 PREP (Preparation); PROC (Process)
 (recovery of hydrogen cyanide from 1,3-butadiene catalytic
 hydrocyanation reaction mixts. in the manufacture of 3-pentenenitriles by
 azeotropic distillation)

IT 16529-56-9P, 2-Methyl-3-butenenitrile
 RL: NUU (Other use, unclassified); PEP (Physical, engineering or chemical
 process); PUR (Purification or recovery); PYP (Physical process); RCT
 (Reactant); PREP (Preparation); PROC (Process); RACT (Reactant or
 reagent); USES (Uses)
 (recovery of hydrogen cyanide from 1,3-butadiene catalytic
 hydrocyanation reaction mixts. in the manufacture of 3-pentenenitriles by
 azeotropic distillation)

IT 74-90-8P, Hydrogen cyanide, preparation
 RL: PEP (Physical, engineering or chemical process); PUR (Purification or
 recovery); PYP (Physical process); RCT (Reactant); PREP
 (Preparation); PROC (Process); RACT (Reactant or reagent)
 (recovery of hydrogen cyanide from 1,3-butadiene catalytic
 hydrocyanation reaction mixts. in the manufacture of 3-pentenenitriles by
 azeotropic distillation)

IT 106-39-0P, 1,3-Butadiene, preparation
 RL: NUU (Other use, unclassified); PEP (Physical, engineering or chemical
 process); PUR (Purification or recovery); PYP (Physical process); RCT
 (Reactant); PREP (Preparation); PROC (Process); RACT (Reactant
 or reagent); USES (Uses)
 (azeotropic distillation agent; recovery of hydrogen cyanide from
 1,3-butadiene catalytic hydrocyanation reaction mixts. in the
 manufacture of 3-pentenenitriles by azeotropic distillation)

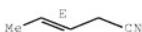
RN 106-99-0 CAPLUS
 CN 1,3-Butadiene (CA INDEX NAME)



IT 16529-66-1P, trans-3-Pentenenitrile
 RL: IMF (Industrial manufacture); PEP (Physical, engineering or chemical
 process); PUR (Purification or recovery); PYP (Physical process);
 PREP (Preparation); PROC (Process)
 (recovery of hydrogen cyanide from 1,3-butadiene catalytic
 hydrocyanation reaction mixts. in the manufacture of 3-pentenenitriles by
 azeotropic distillation)

RN 16529-66-1 CAPLUS
 CN 3-Pentenenitrile, (3E)- (CA INDEX NAME)

Double bond geometry as shown.



IT 74-90-39, Hydrogen cyanide, preparation
 RL: PEP (Physical, engineering or chemical process); PUR (Purification or recovery); PYP (Physical process); PCT (Reactant); PREP (Preparation); PROC (Process); RACT (Reactant or reagent)
 (recovery of hydrogen cyanide from 1,3-butadiene catalytic hydrocyanation reaction mixts. in the manufacture of 3-pentenenitriles by azeotropic distillation)
 RN 74-90-8 CAPLUS
 CN Hydrocyanic acid (CA INDEX NAME)

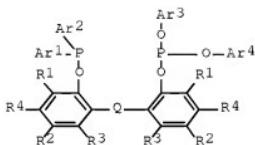


L88 ANSWER 15 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN
 ACCESSION NUMBER: 2005:409533 CAPLUS Full-text
 DOCUMENT NUMBER: 142:430424
 TITLE: Design and preparation of sterically hindered chelate phosphinite-phosphite ligands for nickel-catalyzed preparation of nitriles and dinitriles by hydrocyanation of unsaturated compounds
 INVENTOR(S): Bartsch, Michael; Baumann, Robert; Haderlein, Gerd; Flores, Miguel Angel; Jungkamp, Tim; Luyken, Hermann; Scheidel, Jens; Siegel, Wolfgang
 PATENT ASSIGNEE(S): BASF Aktiengesellschaft, Germany
 SOURCE: PCT Int. Appl., 33 pp.
 CODEN: PIXXD2
 DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|---|------|----------|------------------|----------|
| WO 2005042547 | A1 | 20050512 | WO 2004-EP12176 | 20041028 |
| W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW | | | | |
| RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG | | | | |
| DE 10350999 | A1 | 20050602 | DE 2003-10350999 | 20031030 |
| CA 2543673 | A1 | 20050512 | CA 2004-2543673 | 20041028 |
| EP 1682559 | A1 | 20060726 | EP 2004-790949 | 20041028 |
| R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, FI, RO, CY, TR, BG, CZ, EE, HU, PL, SK | | | | |
| CN 1875025 | A | 20061206 | CN 2004-80032095 | 20041028 |
| BR 2004016080 | A | 20070102 | BR 2004-16080 | 20041028 |
| JP 2007509886 | T | 20070419 | JP 2006-537184 | 20041028 |
| MX 2006PA03939 | A | 20060703 | MX 2006-PA3939 | 20060407 |

| | | | | |
|------------------------|----|----------|------------------|------------|
| US 2007060766 | A1 | 20070315 | US 2006-577138 | 20060425 |
| IN 2006CN01887 | A | 20070223 | IN 2006-CN1887 | 20060529 |
| PRIORITY APPLN. INFO.: | | | DE 2003-10350999 | A 20031030 |
| | | | WO 2004-EP12176 | W 20041028 |

OTHER SOURCE(S): MARPAT 142:430424
GI



I

AB The 2,2'-biphenol, 2,2'-methylenebis(phenol) and 2,2'-binaphthol-bridged phosphinite-phosphite ligands, preferably of the type I (Ar1, Ar2 = Ph, fluoro- and trifluoromethyl-substituted Ph, preferably 3-FC6H4, 3,5-F2C6H3, 3-(CF3)C6H4, 3,5-(CF3)2C6H3; Ar3 = Ar4 = 2-MeC6H4; Q = (CH2)n, where n = 0, 1; R1, R2, R4 = H, C1-8 (un)saturated hydrocarbyl; R3 = H, Me, Et; or R2-R3 = (CH)4, same R1, R2, R4) are designed for nickel(0)-catalyzed hydrocyanation of butadiene to give 3-pentenenitrile and adiponitrile in the presence of Lewis acid promoters, such as metal chlorides and triflates. In an example, ligand of the type I (2, Ar1 = Ar2 = Ph, Ar3 = Ar4 = 2-MeC6H4, R1 = R2 = Me, R3 = R4 = H) was prepared by reaction of 3,3',5,5'-tetramethyl-2,2'-biphenol with Ph2PCl and (2-MeC6H4O)2PCl in toluene at -15°. Hydrocyanation of 1,3-butadiene with HCN catalyzed by Ni(cod)2/2 (1:3 mol. ratio; C4H6/HCN = 1.6:1; 0.135 mol % of the catalyst) gave a 1.5:1 mixture of 2-methyl-3-butenenitrile and 3-pentenenitrile; the ratio was enhanced to 1:4.6 upon isomerization during 1 h at 115°. In another example, 3-pentenenitrile was hydrocyanated to adiponitrile with the same catalyst at 25° for 88 min in the presence of ZnCl2 with regioselectivity of 91.3%. In comparison examples, use of o- and m-tolyl phosphite nickel(0) complex gave only 79.6% selectivity on adiponitrile.

IC ICM C07F009-50**ICS** C07F009-12; B01J031-24**CC** 29-7 (Organometallic and Organometalloidal Compounds)**Section cross-reference(s):** 23

ST phosphorus ligand bidentate diene unsatd nitrile hydrocyanation catalyst; nitrile dinitrile improved prepn process phosphinite phosphite ligand catalyst; nickel catalyzed hydrocyanation phosphinite phosphite bidentate sterically hindered ligand; butadiene pentenenitrile hydrocyanation improved process nickel phosphinite phosphite catalyst; isomerization unsatd nitrile hydrocyanation nickel phosphinite phosphite catalyst; adiponitrile improved prepn regioselective hydrocyanation process nickel catalyst; addn reaction diene unsatd nitrile hydrocyanation adiponitrile improved prepn

IT Ligands

RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);

USES (Uses)

(bidentate, phosphinates, phosphites; design and preparation of sterically hindered phosphinite-phosphite bidentate chelate ligands for nickel-

catalyzed hydrocyanation of dienes and unsatd. nitriles
improved process)

IT Addition reaction
Hydrocyanation
Hydrocyanation catalysts
Regiochemistry
(design and preparation of sterically hindered phosphinite-phosphite
bidentate chelate ligands for nickel-catalyzed hydrocyanation
of dienes and unsatd. nitriles improved process)

IT Chelates
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);
USES (Uses)
(design and preparation of sterically hindered phosphinite-phosphite
bidentate chelate ligands for nickel-catalyzed hydrocyanation
of dienes and unsatd. nitriles improved process)

IT Alkadienes
RL: RCT (Reactant); RACT (Reactant or reagent)
(design and preparation of sterically hindered phosphinite-phosphite
bidentate chelate ligands for nickel-catalyzed hydrocyanation
of dienes and unsatd. nitriles improved process)

IT Steric hindrance
(design and preparation of sterically hindered phosphinite-phosphite
bidentate ligands for nickel-catalyzed hydrocyanation of
dienes and unsatd. nitriles improved process)

IT Nitriles, preparation
RL: SPN (Synthetic preparation); PREP (Preparation)
(dinitriles; design and preparation of sterically hindered
phosphinite-phosphite bidentate chelate ligands for nickel-
catalyzed hydrocyanation of dienes and unsatd. nitriles
improved process)

IT Isomerization
(double bond migration in unsatd. nitriles catalyzed by
sterically hindered phosphinite-phosphite bidentate nickel complexes in
improved process for regioselective hydrocyanation of butadiene)

IT Phosphorus acids
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);
USES (Uses)
(esters, phosphinites; design and preparation of sterically hindered
phosphinite-phosphite bidentate chelate ligands for nickel-
catalyzed hydrocyanation of dienes and unsatd. nitriles
improved process)

IT Phosphites
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);
USES (Uses)
(phosphinites, phosphites; design and preparation of sterically hindered
phosphinite-phosphite bidentate chelate ligands for nickel-
catalyzed hydrocyanation of dienes and unsatd. nitriles
improved process)

IT Nitriles, preparation
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT
(Reactant or reagent)
(unsatd.; isomerization and hydrocyanation of unsatd. nitriles
catalyzed by nickel phosphinite-phosphite bidentate chelate
complexes in adiponitrile improved preparation process)

IT 26567-10-2 110932-47-3
RL: RCT (Reactant); RACT (Reactant or reagent)
(esterification; regioselective hydrocyanation of butadiene and unsatd.
nitriles catalyzed by phosphinite-phosphite bidentate chelate
nickel complexes in improved process for preparation of adiponitrile)

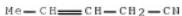
IT 74-90-3, Hydrocyanic acid, reactions 106-99-0,

- 1,3-Butadiene, reactions
 RL: RCT (Reactant); PACT (Reactant or reagent)
 (hydrocyanation; regioselective hydrocyanation of butadiene and unsatd.
 nitriles catalyzed by phosphinite-phosphite bidentate chelate
 nickel complexes in improved process for preparation of adiponitrile)
- IT 592-51-8P, 4-Pentenenitrile
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT
 (Reactant or reagent)
 (hydrocyanation; regioselective hydrocyanation of butadiene and unsatd.
 nitriles catalyzed by phosphinite-phosphite bidentate chelate
 nickel complexes in improved process for preparation of adiponitrile)
- IT 4635-87-4P, 3-Pentenenitrile
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP
 (Preparation); RACT (Reactant or reagent)
 (isomerization, hydrocyanation; regioselective hydrocyanation of
 butadiene and unsatd. nitriles catalyzed by
 phosphinite-phosphite bidentate chelate nickel complexes in improved
 process for preparation of adiponitrile)
- IT 16529-56-9P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT
 (Reactant or reagent)
 (isomerization; regioselective hydrocyanation of butadiene and unsatd.
 nitriles catalyzed by phosphinite-phosphite bidentate chelate
 nickel complexes in improved process for preparation of adiponitrile)
- IT 7440-02-0D, Nickel, complexes, phosphinite-phosphite 7646-85-7, Zinc
 chloride, uses
 RL: CAT (Catalyst use); USES (Uses)
 (regioselective hydrocyanation of butadiene and unsatd. nitriles
 catalyzed by phosphinite-phosphite bidentate chelate nickel
 complexes in improved process for preparation of adiponitrile)
- IT 851024-54-9P 851024-55-0P 851024-56-1P
 RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);
 USES (Uses)
 (regioselective hydrocyanation of butadiene and unsatd. nitriles
 catalyzed by phosphinite-phosphite bidentate chelate nickel
 complexes in improved process for preparation of adiponitrile)
- IT 111-69-3P, Adiponitrile
 RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP
 (Preparation)
 (regioselective hydrocyanation of butadiene and unsatd. nitriles
 catalyzed by phosphinite-phosphite bidentate chelate nickel
 complexes in improved process for preparation of adiponitrile)
- IT 1079-66-9, Chlorodiphenylphosphine 1295-35-8 22277-50-5 33104-14-2
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (regioselective hydrocyanation of butadiene and unsatd. nitriles
 catalyzed by phosphinite-phosphite bidentate chelate nickel
 complexes in improved process for preparation of adiponitrile)
- IT 74-90-8, Hydrocyanic acid, reactions 106-99-0,
 1,3-Butadiene, reactions
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (hydrocyanation; regioselective hydrocyanation of butadiene and unsatd.
 nitriles catalyzed by phosphinite-phosphite bidentate chelate
 nickel complexes in improved process for preparation of adiponitrile)
- RN 74-90-8 CAPLUS
- CN Hydrocyanic acid (CA INDEX NAME)

RN 106-99-0 CAPLUS
 CN 1,3-Butadiene (CA INDEX NAME)



IT 4635-87-4E, 3-Pentenenitrile
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP
 (Preparation); RACT (Reactant or reagent)
 (isomerization, hydrocyanation; regioselective hydrocyanation of
 butadiene and unsatd. nitriles catalyzed by
 phosphinite-phosphite bidentate chelate nickel complexes in improved
 process for preparation of adiponitrile)
 RN 4635-87-4 CAPLUS
 CN 3-Pentenenitrile (CA INDEX NAME)



REFERENCE COUNT: 2 THERE ARE 2 CITED REFERENCES AVAILABLE FOR THIS
 RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L88 ANSWER 16 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN
 ACCESSION NUMBER: 2003:737717 CAPLUS Full-text
 DOCUMENT NUMBER: 139:262467
 TITLE: Phosphonite ligands and their use in hydrocyanation
 INVENTOR(S): Lenges, Christian P.; Lu, Helen S. M.; Ritter, Joachim
 C.
 PATENT ASSIGNEE(S): E. I. Du Pont de Nemours & Co., USA
 SOURCE: PCT Int. Appl., 25 pp.
 CODEN: PIXXD2
 DOCUMENT TYPE: Patent
 LANGUAGE: English
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|--|------|----------|-----------------|----------|
| WO 2003076394 | A1 | 20030918 | WO 2003-US7033 | 20030307 |
| W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW | | | | |
| RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG | | | | |
| US 2003195371 | A1 | 20031016 | US 2002-93655 | 20020307 |
| US 6660877 | B2 | 20031209 | | |

| | | | | |
|------------------------|----|----------|------------------|------------|
| TW 266650 | B | 20061121 | TW 2002-91138062 | 20021231 |
| AU 2003218000 | A1 | 20030922 | AU 2003-218000 | 20030307 |
| US 2003195372 | A1 | 20031016 | US 2003-454074 | 20030604 |
| US 6737539 | B2 | 20040518 | | |
| US 2003212288 | A1 | 20031113 | US 2003-454024 | 20030604 |
| US 6846945 | B2 | 20050125 | | |
| PRIORITY APPLN. INFO.: | | | US 2002-93655 | A 20020307 |
| | | | WO 2003-US7033 | W 20030307 |

OTHER SOURCE(S): MARPAT 139:262467

AB Disclosed herein are processes for hydrocyanation and isomerization of olefins by using at least one multidentate phosphonite ligands, including organometallic phosphonite ligands with a Group VIII metal or Group VIII metal compound, and optionally, a Lewis acid promoter. Thus, trans-3-pentenenitrile was reacted in the presence of bis(1,5- cyclooctadiene) nickel, phosphonite bidentate ligand, and zinc dichloride to give an adiponitrile.

IC ICM C07C253-00

CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)

ST organometallic multidentate phosphonite ligand hydrocyanation catalyst isomerization olefin

IT Hydrocyanation catalysts
Isomerization catalysts
(phosphonite ligands and their use in hydrocyanation)

IT Hydrocyanation catalysts
(stereoselective; phosphonite ligands and their use in hydrocyanation)

IT 111-69-3P, Adiponitrile 592-51-8P, 4-Pentenenitrile 4635-87-4P
, 3-Pentenenitrile 16545-78-1P, cis-3-Pentenenitrile
RL: IMF (Industrial manufacture); PREP (Preparation)
(phosphonite ligands and their use in hydrocyanation)

IT 16529-56-9P, 2-Methyl-3-butenenitrile 16529-66-1P,
trans-3-Pentenenitrile
RL: IMF (Industrial manufacture); RCT (Reactant); PREP
(Preparation); RACT (Reactant or reagent)
(phosphonite ligands and their use in hydrocyanation)

IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,
1,3-Butadiene, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(phosphonite ligands and their use in hydrocyanation)

IT 4635-87-4P, 3-Pentenenitrile 16545-78-1P,
cis-3-Pentenenitrile
RL: IMF (Industrial manufacture); PREP (Preparation)
(phosphonite ligands and their use in hydrocyanation)

RN 4635-87-4 CAPLUS

CN 3-Pentenenitrile (CA INDEX NAME)



RN 16545-78-1 CAPLUS
CN 3-Pentenenitrile, (3Z)- (CA INDEX NAME)

Double bond geometry as shown.



IT 16529-66-1P, trans-3-Pentenenitrile
 RL: IMF (Industrial manufacture); RCT (Reactant); PPEP
 (Preparation); RACT (Reactant or reagent)
 (phosphonite ligands and their use in hydrocyanation)
 RN 16529-66-1 CAPLUS
 CN 3-Pentenenitrile, (3E)- (CA INDEX NAME)

Double bond geometry as shown.



IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,
 1,3-Butadiene, reactions
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (phosphonite ligands and their use in hydrocyanation)
 RN 74-90-8 CAPLUS
 CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 CAPLUS
 CN 1,3-Butadiene (CA INDEX NAME)



| | | |
|-------------------------|--|--|
| REFERENCE COUNT: | 1 | THERE ARE 1 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT |
| L88 ANSWER 17 OF 60 | CAPLUS | COPYRIGHT 2008 ACS on STN |
| ACCESSION NUMBER: | | 2003:223752 CAPLUS Full-text |
| DOCUMENT NUMBER: | | 138:254847 |
| TITLE: | Process for manufacture of nitrile and dinitrile compounds by reaction of alkenes or unsaturated nitriles with hydrogen cyanide in ionic liquid solvents and application to the production of adiponitrile | |
| INVENTOR(S): | Basset, Jean Marie; Chauvin, Yves; Galland, Jean Christophe | |
| PATENT ASSIGNEE(S): | Rhodia Polyamide Intermediates, Fr. | |
| SOURCE: | Fr. Demande, 22 pp. | |
| DOCUMENT TYPE: | Patent | |
| LANGUAGE: | French | |
| FAMILY ACC. NUM. COUNT: | 1 | |
| PATENT INFORMATION: | | |

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|---|------|----------|-----------------|------------|
| FR 2829763 | A1 | 20030321 | FR 2001-12040 | 20010918 |
| FR 2829763 | B1 | 20041203 | | |
| WO 2003024919 | A1 | 20030327 | WO 2002-FR3166 | 20020917 |
| W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG | | | | |
| AU 2002342980 | A1 | 20030401 | AU 2002-342980 | 20020917 |
| EP 1427695 | A1 | 20040616 | EP 2002-779637 | 20020917 |
| R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, SK | | | | |
| CN 1564807 | A | 20050112 | CN 2002-819851 | 20020917 |
| JP 2005503410 | T | 20050203 | JP 2003-528767 | 20020917 |
| RU 2265591 | C2 | 20051210 | RU 2004-111655 | 20020917 |
| IN 2004CN00554 | A | 20051223 | IN 2004-CN554 | 20040315 |
| US 2004260112 | A1 | 20041223 | US 2004-489838 | 20040818 |
| PRIORITY APPLN. INFO.: | | | FR 2001-12040 | A 20010918 |
| | | | WO 2002-FR3166 | W 20020917 |

OTHER SOURCE(S): CASREACT 138:254847

AB The invention relates to the manufacture of nitriles from unsatd. organic compds. by reaction with HCN. In particular, it relates to manufacture of nitriles used in the synthesis of adiponitrile, an important chemical intermediate for the manufacture of, e.g., hexamethylenediamine and ϵ -caprolactam. The process provides compds. containing ≥ 1 nitrile function by hydrocyanation, with HCN, of an organic compound containing ≥ 1 ethylenic unsatn. The reaction takes place in the presence of a catalytic system comprising nickel, platinum, or palladium, and an organophosphorus ligand, using an ionic liquid reaction medium. A Lewis acid cocatalyst, functioning as an isomerization catalyst for unsatd. nitriles, may also be present. This cocatalyst provides for isomerization of undesired branched unsatd. nitriles to give preferred linear isomers, which undergo hydrocyanation to give adiponitrile. The anion of the ionic solvent may also function as a Lewis acid. For instance, the ionic liquid 1-butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)amide (I) was prepared in 90% yield from the corresponding imidazolium chloride and lithium amide salts in water at room temperature I and 2 other imidazolium salts were prepared and tested as solvents and isomerization catalysts in a representative hydrocyanation reaction mixture. Thus, a mixture of unsatd. C5 nitriles containing 79% 2-methyl-3-butenenitrile (II) was subjected to isomerization in a solution of I and heptane in the presence of Ni(COD)2 (hydrocyanation catalyst) and 3-(Ph2P)CH2SO3Na (ligand) at 100° for 3 h. The isomerization reaction gave 96% conversion of II, with a 94% yield of the desired linear isomers 3-pentenonitrile (III) and 4-pentenonitrile, with only 2.4% yield of undesired isomers. In a hydrocyanation reaction of III using the same catalyst and ligand, I as solvent, Me2C(OH)CN as the source of HCN, and added ZnCl2 as an addnl. Lewis acid, desired dinitrile products (including adiponitrile) were obtained in 16.0% yield with 25.9% conversion of III.

ICM C07C255-04

CC 23-19 (Aliphatic Compounds)

Section cross-reference(s): 45

ST nitrile unsatd hydrocyanation hydrogen cyanide liq ionic solvent; imidazolium ionic liq solvent hydrocyanation pentenenitrile; adiponitrile manuf ionic liq solvent imidazolium; isomerization methylbutenenitrile pentenenitrile Lewis acid catalyst; nickel palladium platinum phosphine ligand hydrocyanation catalyst ionic solvent

IT Isomerization catalysts
 (Lewis acids; process for manufacture of nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents)

IT Ligands
 RL: CAT (Catalyst use); RCT (Reactant); RACT (Reactant or reagent); USES (Uses)
 (hydrocyanation catalyst component; process for manufacture of nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents)

IT Lewis acids
 RL: CAT (Catalyst use); USES (Uses)
 (isomerization cocatalyst; process for manufacture of nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents)

IT Hydrocyanation catalysts
 (nickel, platinum, or palladium with organophosphorus ligands; process for manufacture of nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents)

in
 Organic compounds, reactions
 RL: CAT (Catalyst use); RCT (Reactant); RACT (Reactant or reagent); USES (Uses)
 (phosphorus-containing, hydrocyanation catalyst ligands; process for manufacture of nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents)

IT 122-52-1, Triethyl phosphite 603-35-0, Triphenylphosphine, reactions 607-01-2, Diphenylethylphosphine 672-66-2, Dimethylphenylphosphine 855-38-9, Tris(p-methoxyphenyl)phosphine 998-40-3, Tributylphosphine 2622-14-2, Tricyclohexylphosphine 4712-55-4, Diphenyl phosphite 7688-25-7, 1,4-Bis(diphenylphosphino)butane 26834-21-9, Tritolylphosphine 34684-16-7, Dimethyl-n-octylphosphine 63995-75-5, Sodium triphenylphosphinomonoo-m-sulfonate 226420-48-0, (3-Sodiosulfonatophenyl)diphenylphosphine 250788-83-1, (5-Sodiocarboxy-2-furyl)diphenylphosphine
 RL: CAT (Catalyst use); RCT (Reactant); RACT (Reactant or reagent); USES (Uses)
 (hydrocyanation catalyst ligand; process for manufacture of nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents)

IT 1295-35-8, Di(1,5-cyclooctadiene)nickel 7440-02-0, Nickel, uses 7440-05-3, Palladium, uses 7440-06-4, Platinum, uses
 RL: CAT (Catalyst use); USES (Uses)
 (hydrocyanation catalyst; process for manufacture of nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents)

IT 106-99-0, 1,3-Butadiene, reactions
 RL: RCT (Reactant); PACT (Reactant or reagent)
 (hydrocyanation substrate; process for manufacture of nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents)

IT 960-71-4, Triphenylborane 1078-58-6, Diphenylzinc 7646-79-9, Cobalt dichloride, uses 7646-85-7, Zinc chloride, uses 54010-75-2, Zinc triflate 128008-30-0, Indium triflate
 RL: CAT (Catalyst use); USES (Uses)
 (isomerization cocatalyst; process for manufacture of nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents)

IT 592-51-8P, 4-Pentenenitrile 4635-87-4P, 3-Pentenenitrile

RL: IMF (Industrial manufacture); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
 (isomerization product and hydrocyanation substrate; process for manufacture
 of nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents)

IT 74-90-8, Hydrogen cyanide, reactions
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (process for manufacture of nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents)

IT 106-99-0, 1,3-Butadiene, reactions
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (hydrocyanation substrate; process for manufacture of nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents)

RN 106-99-0 CAPLUS
 CN 1,3-Butadiene (CA INDEX NAME)



IT 4635-87-4P, 3-Pentenenitrile
 RL: IMF (Industrial manufacture); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
 (isomerization product and hydrocyanation substrate; process for manufacture
 of nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents)

RN 4635-87-4 CAPLUS
 CN 3-Pentenenitrile (CA INDEX NAME)



IT 74-90-8, Hydrogen cyanide, reactions
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (process for manufacture of nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents)

RN 74-90-8 CAPLUS
 CN Hydrocyanic acid (CA INDEX NAME)



REFERENCE COUNT: 4 THERE ARE 4 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L88 ANSWER 18 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN
 ACCESSION NUMBER: 2003:93132 CAPLUS [Full-text](#)
 DOCUMENT NUMBER: 138:137726

TITLE: Isomerization and hydrocyanation of monoolefinic C5-mononitriles in the presence of Ni(0)-phosphite/phosphonite catalysts

INVENTOR(S): Bartsch, Michael; Baumann, Robert; Kunsmann-Keitel, Dagmar Pascale; Haderlein, Gerd; Jungkamp, Tim; Altmayer, Marco; Siegel, Wolfgang

PATENT ASSIGNEE(S): BASF AG, Germany

SOURCE: Ger. Offen., 18 pp.

CODEN: GWXXBX

DOCUMENT TYPE: Patent

LANGUAGE: German

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|---|------|----------|------------------|------------|
| DE 10136488 | A1 | 20030206 | DE 2001-10136488 | 20010727 |
| TW 570839 | B | 20040111 | TW 2002-91115419 | 20020711 |
| CA 2454912 | A1 | 20030213 | CA 2002-2454912 | 20020716 |
| WO 2003011457 | A1 | 20030213 | WO 2002-EP7888 | 20020716 |
| W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW | | | | |
| RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG | | | | |
| AU 2002355640 | A1 | 20030217 | AU 2002-355640 | 20020716 |
| EP 1414567 | A1 | 20040506 | EP 2002-791454 | 20020716 |
| R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, SK | | | | |
| BR 2002011455 | A | 20040817 | BR 2002-11455 | 20020716 |
| CN 1535179 | A | 20041006 | CN 2002-814769 | 20020716 |
| JP 2004535929 | T | 20041202 | JP 2003-516681 | 20020716 |
| MX 2004PA00559 | A | 20040420 | MX 2004-PA559 | 20040119 |
| US 2004176622 | A1 | 20040909 | US 2004-484169 | 20040120 |
| IN 2004CN00391 | A | 20051223 | IN 2004-CN391 | 20040226 |
| PRIORITY APPLN. INFO.: | | | DE 2001-10136488 | A 20010727 |
| | | | WO 2002-EP7888 | W 20020716 |

OTHER SOURCE(S): MARPAT 138:137726

AB Monoolefinic C5-mononitriles, e.g., 2-methyl-3-butenenitrile (readily available from hydrocyanation of 1,3-butadiene), was isomerized into a mixture of linear mononitrile, e.g., 3-pentenenitrile (main) with improved selectivity in the presence of Ni(0) complexes with chelating bisphosphite or bisphosphonite ligands. The pentenenitrile isomers can be further hydrocyanated with HCN to the corresponding dinitriles, e.g., adiponitrile, with the same catalysts and ZnCl₂ promoter.

IC ICM B01J031-22

ICS B01J031-24; C07C253-10; C07B043-08

CC 35-2 (Chemistry of Synthetic High Polymers)

Section cross-reference(s): 67

ST monoolefinic nitrile isomerization hydrocyanation dinitrile manuf; nickel phosphite catalyst nitrile isomerization hydrocyanation; phosphonite nickel catalyst nitrile isomerization hydrocyanation

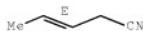
IT Hydrocyanation catalysts

Isomerization catalysts
(catalysts for isomerization and hydrocyanation of nitriles)

10/586490

- IT Hydrocyanation
Isomerization
(production of dinitrile monomers from olefinic mononitriles by catalytic isomerization and hydrocyanation)
- IT Nitriles, preparation
RL: IMF (Industrial manufacture); PREP (Preparation)
(production of dinitrile monomers from olefinic mononitriles by catalytic isomerization and hydrocyanation)
- IT 1295-35-8, Bis(1,5-cyclooctadienyl)nickel
RL: CAT (Catalyst use); USES (Uses)
(catalyst precursor; catalysts for isomerization and hydrocyanation of nitriles)
- IT 7646-85-7, Zinc chloride, uses
RL: CAT (Catalyst use); USES (Uses)
(catalyst promoter; catalysts for isomerization and hydrocyanation of nitriles)
- IT 620-38-2D, Tris(m-Tolyl)phosphite, complex with nickel 620-42-8D, p-Tolylphosphite, complex with nickel 7440-02-0D, Nickel, complexes with phosphite ligands 179259-60-0D, complex with nickel 220472-84-4D, complex with nickel 494227-34-8D, complex with nickel 620-42-8D, RL: CAT (Catalyst use); USES (Uses)
(catalysts for isomerization and hydrocyanation of nitriles)
- IT 111-69-3P, Adipodinitrile 16529-66-1P, trans-3-Pentenenitrile 16545-78-1P, cis-3-Pentenenitrile 20068-02-4P, cis-2-Methyl-2-butenenitrile 25899-50-7P, cis-2-Pentenenitrile 26294-98-4P, trans-2-Pentenenitrile 28906-50-5P, Methylglutaronitrile 30574-97-1P, trans-2-Methyl-2-butenenitrile 30574-97-1P, trans-2-Methyl-2-butenenitrile 30574-97-1P, RL: IMF (Industrial manufacture); PREP (Preparation)
(production of dinitrile monomers from olefinic mononitriles by catalytic isomerization and hydrocyanation)
- IT 4635-87-4P, 3-Pentenenitrile
RL: IMF (Industrial manufacture); RCT (Reactant); PREP (Preparation); RACT (Reactant or reagent)
(production of dinitrile monomers from olefinic mononitriles by catalytic isomerization and hydrocyanation)
- IT 74-90-8, Hydrocyanic acid, reactions 106-99-0, 1,3-Butadiene, reactions 16529-56-9, 2-Methyl-3-butenenitrile
RL: RCT (Reactant); RACT (Reactant or reagent)
(production of dinitrile monomers from olefinic mononitriles by catalytic isomerization and hydrocyanation)
- IT 16529-66-1P, trans-3-Pentenenitrile 16545-78-1P, cis-3-Pentenenitrile
RL: IMF (Industrial manufacture); PREP (Preparation)
(production of dinitrile monomers from olefinic mononitriles by catalytic isomerization and hydrocyanation)
- RN 16529-66-1 CAPLUS
- CN 3-Pentenenitrile, (3E)- (CA INDEX NAME)

Double bond geometry as shown.



RN 16545-78-1 CAPLUS
CN 3-Pentenenitrile, (3Z)- (CA INDEX NAME)

Double bond geometry as shown.



IT 4635-87-4E, 3-Pentenenitrile

RL: IMF (Industrial manufacture); RCT (Reactant); PREP (Preparation); RACT (Reactant or reagent)
 (production of dinitrile monomers from olefinic mononitriles by catalytic isomerization and hydrocyanation)

RN 4635-87-4 CAPLUS

CN 3-Pentenenitrile (CA INDEX NAME)



IT 74-90-8, Hydrocyanic acid, reactions 106-99-0,

1,3-Butadiene, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)
 (production of dinitrile monomers from olefinic mononitriles by catalytic isomerization and hydrocyanation)

RN 74-90-8 CAPLUS

CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 CAPLUS

CN 1,3-Butadiene (CA INDEX NAME)



L88 ANSWER 19 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 2002:888694 CAPLUS Full-text

DOCUMENT NUMBER: 1371371731

TITLE: Copper-catalyzed, vapor-phase hydrocyanation process for the conversion of diolefinic compounds with hydrogen cyanide into unsaturated nitriles

INVENTOR(S): Drulinier, Joe Douglas; Herron, Norman; Lecloux, Daniel E. I. Du Pont de Nemours & Co., USA; Harmer, Mark Andrew

PATENT ASSIGNEE(S): PCT Int. Appl., 18 pp.
CODEN: PIXXD2

SOURCE: Patent

DOCUMENT TYPE: English
LANGUAGE:

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|---|------|----------|------------------|------------|
| WO 2002092551 | A2 | 20021121 | WO 2002-US14607 | 20020510 |
| WO 2002092551 | A3 | 20030213 | | |
| W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW | | | | |
| RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG | | | | |
| US 2003045740 | A1 | 20030306 | US 2002-140736 | 20020508 |
| US 6753440 | B2 | 20040622 | | |
| CA 2447051 | A1 | 20021121 | CA 2002-2447051 | 20020510 |
| AU 2002308654 | A1 | 20021125 | AU 2002-308654 | 20020510 |
| EP 1395547 | A2 | 20040310 | EP 2002-769693 | 20020510 |
| EP 1395547 | B1 | 20050316 | | |
| R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR | | | | |
| TW 580489 | B | 20040321 | TW 2002-91109774 | 20020510 |
| JP 2004534032 | T | 20041111 | JP 2002-589437 | 20020510 |
| MX 2003PA10214 | A | 20040310 | MX 2003-PA10214 | 20031107 |
| PRIORITY APPLN. INFO.: | | | US 2001-290294P | P 20010511 |
| | | | WO 2002-US14607 | W 20020510 |

OTHER SOURCE(S): MARPAT 137:371731

- AB A catalyzed, vapor-phase process for the hydrocyanation of acyclic diolefinic compds. (e.g., butadiene) to olefinic nitriles (e.g., pentenenitriles) with HCN is described in which the product's olefinic double bond is not conjugated to the triple bond of the cyano group and where a catalyst composition comprising supported copper salts (e.g., cupric triflate/C) is used.
- IC ICM C07C253-10
ICS C07C255-07
- CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)
Section cross-reference(s): 23, 48, 67
- ST butadiene gas phase hydrocyanation pentenenitrile manuf; supported copper catalyst diene hydrocyanation unsatd nitrile manuf
- IT Alkadienes
RL: RCT (Reactant); RACT (Reactant or reagent)
(copper-catalyzed vapor-phase hydrocyanation process for the conversion of diolefinic compds. into unsatd. nitriles)
- IT Hydrocyanation catalysts
(supported copper compds. in a vapor-phase hydrocyanation process for the conversion of diolefinic compds. into unsatd. nitriles)
- IT Nitriles, preparation
RL: IMF (Industrial manufacture); PREP (Preparation)
(unsatd.; copper-catalyzed vapor-phase hydrocyanation process for the conversion of diolefinic compds. into unsatd. nitriles)
- IT 7440-44-0, Activated carbon, uses
RL: CAT (Catalyst use); USES (Uses)
(activated, support; copper-compound hydrocyanation catalysts in a vapor-phase hydrocyanation process for the conversion of diolefinic compds. into unsatd. nitriles)
- IT 592-51-8P, 4-Pentenenitrile 1647-11-6P, 2-Cyano-1-butene 4635-87-4P
, 3-Pentenenitrile

IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,
 Butadiene, reactions
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (copper-catalyzed vapor-phase hydrocyanation process for the conversion of diolefinic compds. with hydrogen cyanide into unsatd. nitriles)

IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,
 Butadiene, reactions
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (copper-catalyzed vapor-phase hydrocyanation process for the conversion of diolefinic compds. with hydrogen cyanide into unsatd. nitriles)

IT 34946-82-2, Cupric triflate 42152-44-3, Cuprous triflate
 RL: CAT (Catalyst use); USES (Uses)
 (hydrocyanation catalysts in a vapor-phase hydrocyanation process for the conversion of diolefinic compds. into unsatd. nitriles)

IT 1344-28-1, Alumina, uses 7631-86-9, Silica, uses
 RL: CAT (Catalyst use); USES (Uses)
 (support; copper-compound hydrocyanation catalysts in a vapor-phase hydrocyanation process for the conversion of diolefinic compds. into unsatd. nitriles)

IT 4635-87-4P, 3-Pentenenitrile
 RL: IMF (Industrial manufacture); PREP (Preparation)
 (copper-catalyzed vapor-phase hydrocyanation process for the conversion of diolefinic compds. with hydrogen cyanide into unsatd. nitriles)

RN 4635-87-4 CAPLUS
 CN 3-Pentenenitrile (CA INDEX NAME)



IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,
 Butadiene, reactions
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (copper-catalyzed vapor-phase hydrocyanation process for the conversion of diolefinic compds. with hydrogen cyanide into unsatd. nitriles)

RN 74-90-8 CAPLUS
 CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 CAPLUS
 CN 1,3-Butadiene (CA INDEX NAME)



IT 1344-28-1, Alumina, uses

RL: CAT (Catalyst use); USES (Uses)
 (support; copper-compound hydrocyanation catalysts in a
 vapor-phase hydrocyanation process for the conversion of diolefinic
 compds. into unsatd. nitriles)

RN 1344-28-1 CAPLUS
 CN Aluminum oxide (Al2O3) (CA INDEX NAME)

*** STRUCTURE DIAGRAM IS NOT AVAILABLE ***

L88 ANSWER 20 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN
 ACCESSION NUMBER: 2002:293580 CAPLUS Full-text
 DOCUMENT NUMBER: 136:327370
 TITLE: Hydrocyanation method and catalyst systems for
 converting ethylenically unsaturated organic compounds
 into nitriles
 INVENTOR(S): Burattin, Paolo; Galland, Jean-Christophe; Chamard,
 Alex
 PATENT ASSIGNEE(S): Rhodia Polyamide Intermediates, Fr.
 SOURCE: PCT Int. Appl., 24 pp.
 CODEN: PIXXD2
 DOCUMENT TYPE: Patent
 LANGUAGE: French
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|--|------|----------|------------------|------------|
| WO 2002030854 | A2 | 20020418 | WO 2001-FR3047 | 20011003 |
| WO 2002030854 | A3 | 20020613 | | |
| W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KE, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW | | | | |
| RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG | | | | |
| FR 2815344 | A1 | 20020419 | FR 2000-13152 | 20001013 |
| FR 2815344 | B1 | 20040130 | | |
| TW 584623 | B | 20040421 | TW 2001-90124118 | 20010928 |
| CA 2425384 | A1 | 20020418 | CA 2001-2425384 | 20011003 |
| AU 2001095653 | A | 20020422 | AU 2001-95653 | 20011003 |
| EP 1324976 | A2 | 20030709 | EP 2001-976353 | 20011003 |
| EP 1324976 | B1 | 20060201 | | |
| R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR | | | | |
| BR 2001014807 | A | 20040106 | BR 2001-14807 | 20011003 |
| HU 2003003560 | A2 | 20040301 | HU 2003-3560 | 20011003 |
| JP 2004511450 | T | 20040415 | JP 2002-534244 | 20011003 |
| RU 2250896 | C2 | 20050427 | RU 2003-113534 | 20011003 |
| AT 316955 | T | 20060215 | AT 2001-976353 | 20011003 |
| MX 2003PA03107 | A | 20040126 | MX 2003-PA3107 | 20030409 |
| US 2004063956 | A1 | 20040401 | US 2003-399237 | 20030924 |
| US 7098358 | B2 | 20060829 | | |
| PRIORITY APPLN. INFO.: | | | FR 2000-13152 | A 20001013 |
| | | | WO 2001-FR3047 | W 20011003 |

OTHER SOURCE(S): MARPAT 136:327370
 AB A method for hydrocyanation of ethylenically unsatd. organic compds. into
 compds. comprising at least a nitrile function comprises the reaction of

- hydrogen cyanide in the presence of a catalytic system comprising a transition metal and an organophosphorus ligand with monophosphanorbornadiene structure and the process is particularly useful for the hydrocyanation of butadiene into adiponitrile.
- IC ICM C07C
- CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)
Section cross-reference(s): 23, 29, 67
- ST alkene hydrocyanation nitrile prepn; butadiene hydrocyanation isomerization manuf adiponitrile; monophosphanorbornadiene ligand catalyst butadiene hydrocyanation isomerization manuf adiponitrile
- IT Nitriles, preparation
RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)
(aliphatic; hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)
- IT Rare earth halides
RL: CAT (Catalyst use); USES (Uses)
(bromides; in hydrocyanation catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)
- IT Nitriles, preparation
RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)
(dinitriles, aliphatic; hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)
- IT Alkadienes
RL: RCT (Reactant); RACT (Reactant or reagent)
(hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)
- IT Group IB elements
Group IIB elements
Group IIIA elements
Group IIIB elements
Group IVA elements
Group IVB elements
Group VA elements
Group VB elements
Group VIB elements
Group VIIIB elements
Group VIII elements
Lewis acids
Rare earth chlorides
Transition metals, uses
RL: CAT (Catalyst use); USES (Uses)
(in hydrocyanation catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)
- IT Phosphines
Phosphites
Phosphoranes
RL: CAT (Catalyst use); USES (Uses)
(monophosphanorbornadienes; in hydrocyanation catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)
- IT Nitriles, preparation
RL: IMF (Industrial manufacture); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(unsatd., aliphatic; hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)
- IT Alkenes, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)

- (α -; hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)
- IT 110-59-8P, Valeronitrile 111-69-3P, Adiponitrile 4553-62-2P,
2-Methylglutaronitrile 17611-82-4P
RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)
(hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)
- IT 78-79-5, Isoprene, reactions 106-99-0, Butadiene, reactions 111-78-4, 1,5-Cyclooctadiene 592-42-7, 1,5-Hexadiene
RL: PCT (Reactant); PACT (Reactant or reagent)
(hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)
- IT 592-51-8P, 4-Pentenenitrile 4403-61-6P, 2-Methyl-2-butenenitrile 4635-87-4P, 3-Pentenenitrile 16529-56-9P, 2-Methyl-3-butenenitrile
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)
- IT 98-83-9P, Methylstyrene, preparation 100-42-5P, Styrene, preparation 110-83-8P, Cyclohexene, preparation 1335-86-0P, Methylcyclohexene 26588-32-9P, Vinylnaphthalene
RL: SPN (Synthetic preparation); PREP (Preparation)
(hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)
- IT 74-90-8, Hydrogen cyanide, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles using)
- IT 815-85-0, Stannous tartrate 1295-35-8, Nickel bis(1,5-cyclooctadiene) 3333-67-3, Nickel carbonate 3349-06-2, Nickel formate 7439-89-6, Iron, uses 7440-05-3, Palladium, uses 7488-55-3, Stannous sulfate 7646-79-9, Cobalt chloride, uses 7646-85-7, Zinc chloride, uses 7699-45-8, Zinc bromide 7718-54-9, Nickel chloride, uses 7758-94-3, Ferrous chloride 7772-99-8, Stannous chloride, uses 7773-01-5, Manganese chloride 7786-81-4, Nickel sulfate 7789-42-6, Cadmium bromide 10031-24-0, Stannous bromide 10108-64-2, Cadmium chloride 10139-47-6, Zinc iodide 10361-92-9, Yttrium chloride 10381-36-9, Nickel phosphate 12054-48-7, Nickel hydroxide 12266-58-9, Nickel bisacrylonitrile 12738-03-3, Manganese bromide 13138-45-9, Nickel nitrate 13462-88-9, Nickel bromide 13462-90-3, Nickel iodide 13689-92-4, Nickel thiocyanate 14220-17-8, Potassium tetracyannickelate 14332-33-3, Nickel phosphite 15133-82-1, Tetrakis(triphenylphosphine)nickel 16812-54-7, Nickel(II) sulfide 17237-93-3, Nickel bicarbonate 22605-92-1, Nickel citrate 38150-64-0, Cyanic acid, nickel(2+) salt 51142-85-9, Nickel borate 128008-30-0, Indium(III) triflate
RL: CAT (Catalyst use); USES (Uses)
(in hydrocyanation catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)
- IT 106-99-0, Butadiene, reactions
RL: PCT (Reactant); PACT (Reactant or reagent)
(hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)
- RN 106-99-0 CAPLUS
CN 1,3-Butadiene (CA INDEX NAME)



IT 4635-87-4P, 3-Pentenenitrile
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP
 (Preparation); RACT (Reactant or reagent)
 (hydrocyanation method and catalyst systems for converting
 ethylenically unsatd. organic compds. into nitriles)
 RN 4635-87-4 CAPLUS
 CN 3-Pentenenitrile (CA INDEX NAME)



IT 74-90-3, Hydrogen cyanide, reactions
 RL: PCT (Reactant); FACT (Reactant or reagent)
 (hydrocyanation method and catalyst systems for converting
 ethylenically unsatd. organic compds. into nitriles using)
 RN 74-90-8 CAPLUS
 CN Hydrocyanic acid (CA INDEX NAME)



L88 ANSWER 21 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN
 ACCESSION NUMBER: 2001:228948 CAPLUS [Full-text](#)
 DOCUMENT NUMBER: 134:266726
 TITLE: Polymeric phosphite catalysts for hydrocyanation of
 unsaturated organic compounds and isomerization of
 unsaturated nitriles
 INVENTOR(S): Tam, Wilson; Kristjansdottir, Sigridur Soley; Greene,
 Robin Nikolas
 PATENT ASSIGNEE(S): E. I. Du Pont de Nemours & Co., USA
 SOURCE: PCT Int. Appl., 48 pp.
 CODEN: PIXXD2
 DOCUMENT TYPE: Patent
 LANGUAGE: English
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|---|------|----------|-----------------|----------|
| WO 2001021684 | A1 | 20010329 | WO 2000-US25568 | 20000919 |
| W: BR, CA, CN, CZ, ID, JP, KR, MX, PL, SG, SK | | | | |
| RW: AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE | | | | |
| US 6284865 | B1 | 20010904 | US 1999-399261 | 19990920 |
| CA 2384408 | A1 | 20010329 | CA 2000-2384408 | 20000919 |
| BR 2000014478 | A | 20020618 | BR 2000-14478 | 20000919 |
| EP 1216268 | A1 | 20020626 | EP 2000-963590 | 20000919 |
| EP 1216268 | B1 | 20031112 | | |
| R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, | | | | |

IE, FI, CY

| | | | | |
|---------------|----|----------|---|---|
| CN 1390241 | A | 20030108 | CN 2000-815657 | 20000919 |
| JP 2003510385 | T | 20030318 | JP 2001-525254 | 20000919 |
| CN 1847288 | A | 20061018 | CN 2006-10081921 | 20000919 |
| TW 226345 | B | 20050111 | TW 2000-89119359 | 20000920 |
| US 2001049431 | A1 | 20011206 | US 2001-865942 | 20010525 |
| US 6855799 | B2 | 20050215 | | |
| HK 1052364 | A1 | 20070511 | HK 2003-104699 US 1999-399261 CN 2000-815657 WO 2000-US25568 | 20030702 A 19990920 A3 20000919 W 20000919 |

PRIORITY APPLN. INFO.:

AB A polymeric composition, a process for producing the composition, and a process for using the composition in, for example, hydrocyanation or isomerization are disclosed. The composition comprises repeat units derived from (1) a carbonyl compound, a monomer, and phosphorochloridite; (2) phosphorus trichloride, a polyhydric alc., and an aromatic diol; or (3) combinations of (1) and (2) in which the monomer can be a polyhydric alc., an amine, combinations thereof. The composition can further comprise a Group VIII metal and optionally a Lewis acid. The composition can be produced by (1) contacting a carbonyl compound with the monomer to produce an intermediate and contacting the intermediate with phosphorochloridite; (2) contacting phosphorus trichloride with a second polyhydric alc. under a condition sufficient to produce a phosphorus-containing polymer and contacting the phosphorus-containing polymer with an aromatic diol; or (3) contacting an N,N-dialkyl dichlorophosphoramidite with a second polyhydric alc. to produce a polymer phosphoramidite, contacting the polymer phosphoramidite with an acid such as HCl to produce the phosphorus-containing polymer, which is then contacted with an aromatic diol. The composition can be used as catalyst, for example, for converting an unsatd. organic compound to a nitrile and isomerizing a nitrile.

IC ICM C08G069-48

ICS C08G063-91; C08G079-04; B01J031-18

CC 35-5 (Chemistry of Synthetic High Polymers)

ST polyester phosphite hydrocyanation catalyst; polyamide phosphite hydrocyanation catalyst

IT Hydrocyanation catalysts
Isomerization catalysts

(polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)

IT Polyanimides, preparation

Polyesters, preparation

RL: CAT (Catalyst use); IMF (Industrial manufacture); PREP (Preparation); USES (Uses)

(polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)

IT 1295-35-8

RL: CAT (Catalyst use); USES (Uses)

(polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)

IT 90-02-8DP, Salicylaldehyde, acetals with propanediol, phospho-containing polyesters 504-63-2DP, 1,3-Propanediol, acetals with salicylaldehyde, phospho-containing polyesters 331677-94-2DP, reaction products with o-Cresol phosphorochloridite 331677-99-7P 331722-26-0P

RL: CAT (Catalyst use); IMF (Industrial manufacture); PREP (Preparation); USES (Uses)

(polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)

IT 4635-97-4F, 3-Pentenenitrile 16529-56-9P, 2-Methyl-3-butenenitrile

RL: IMF (Industrial manufacture); PREP (Preparation)

(polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)

IT 331677-94-2P, Dimethyl 2,2'-dihydroxy-1,1'-binaphthalene-3,3'-dicarboxylate-1,6-hexanediol copolymer 331722-22-6P 331722-23-7P
331722-24-8DP, reaction products with o-Cresol phosphorochloridite 331722-24-8P 331722-25-9P
RL: IMF (Industrial manufacture); RCT (Reactant); PREP (Preparation); RACT (Reactant or reagent)
(polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)

IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,
Butadiene, reactions 592-51-8, 4-Pentenenitrile 818-57-5, Methyl 4-pentenoate 818-58-6, Methyl 3-pentenoate 818-59-7, Methyl 2-pentenoate
RL: RCT (Reactant); RACT (Reactant or reagent)
(polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)

IT 4635-87-4P, 3-Pentenenitrile
RL: IMF (Industrial manufacture); PREP (Preparation)
(polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)

RN 4635-87-4 CAPLUS
CN 3-Pentenenitrile (CA INDEX NAME)



IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,
Butadiene, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)

RN 74-90-8 CAPLUS
CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 CAPLUS
CN 1,3-Butadiene (CA INDEX NAME)



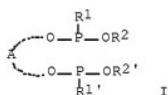
REFERENCE COUNT: 3 THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L88 ANSWER 22 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 1999:791822 CAPLUS Full-text

DOCUMENT NUMBER: 132:37251
 TITLE: Group VIII metal complex catalyst with bidentate phosphonite ligand, and method for preparing nitriles
 INVENTOR(S): Fischer, Jakob; Siegel, Wolfgang; Keitel, Dagmar Pascale; Siggel, Lorenz
 PATENT ASSIGNEE(S): BASF A.-G., Germany
 SOURCE: Ger. Offen., 18 pp.
 CODEN: GWXXBX
 DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|--|------|----------|------------------|------------|
| DE 19825212 | A1 | 19991209 | DE 1998-19825212 | 19980605 |
| TW 519496 | B | 20030201 | TW 1999-88109210 | 19990603 |
| CA 2334151 | A1 | 19991216 | CA 1999-2334151 | 19990604 |
| CA 2334151 | C | 20071023 | | |
| WO 9964155 | A1 | 19991216 | WO 1999-EP3888 | 19990604 |
| W: AE, BR, CA, CN, CZ, ID, IN, JP, KR, MX, RU, SG, TR, US | | | | |
| RW: AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE | | | | |
| BR 9910956 | A | 20010313 | BR 1999-10956 | 19990604 |
| EP 1091804 | A1 | 20010418 | EP 1999-927883 | 19990604 |
| EP 1091804 | B1 | 20020227 | | |
| R: BE, DE, ES, FR, GB, IT, NL | | | | |
| TR 200003625 | T2 | 20010420 | TR 2000-3625 | 19990604 |
| JP 2002517473 | T | 20020618 | JP 2000-553209 | 19990604 |
| ES 2173750 | T3 | 20021016 | ES 1999-927883 | 19990604 |
| RU 2223146 | C2 | 20040210 | RU 2001-101148 | 19990604 |
| MX 2000PA11522 | A | 20010521 | MX 2000-PA11522 | 20001123 |
| US 6521778 | B1 | 20030218 | US 2000-701601 | 20001130 |
| IN 2000CN00891 | A | 20050722 | IN 2000-CN891 | 20050722 |
| PRIORITY APPLN. INFO.: | | | DE 1998-19825212 | A 19980605 |
| | | | WO 1999-EP3888 | W 19990604 |

OTHER SOURCE(S): MARPAT 132:37251
 GI



AB A catalyst useful for the manufacture of mixts. of C5-monoolefinic nitriles with the double bond nonconjugated with nitrile group by hydrocyanation of dienes and for isomerization of branched aliphatic monoalkenenitriles into linear monoalkenenitriles comprises a group VIII metal complex with P-containing ligands (structures specified). A process for the manufacture of adipic acid dinitrile by hydrocyanation of 1,3-butadiene followed by isomerization of the resulting mixture of monoolefinic C5-mononitriles is also claimed. For example, a mixture of 0.41 g bis(1,5-cyclooctadiene)nickel and 2.14 g ligand I and 10 mL PhMe was placed in a glass autoclave under Ar, stirred for 10 min, a mixture of 7.9 g 1,3-butadiene and 40 g PhMe was added,

the mixture was heated at 70° (pressure increased to 1.2 bar), treated over 90 min with a mixture of 3.2 g HCN and 40 g PhMe (pressure dropped to 0.5 bar) and the whole allowed to react for 120 min at 70° to give a product containing 99.4% of a mixture of MeCH:CHCH₂CN (II), CH₂:CHCH₂CH₂CN and CH₂:CHCHMeCN (III) with II:III ratio of 0.41:1. II:III ratio can be increased by extending the reaction duration time after HCN addition was completed.

- IC ICM B01J031-22
 ICS C07F009-40; C07C253-10; C07C255-06; C07C255-04
 CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)
 Section cross-reference(s): 67
 ST hydrocyanation catalyst alkenenitrile manuf butadiene; butadiene hydrocyanation cyclooctadienickel complex catalyst phosphonite ligand; hydrocyanic acid hydrocyanation butadiene cyclooctadienickel complex catalyst phosphonite ligand; methylbutenenitrile manuf cyclooctadienickel complex catalyst phosphonite ligand; pentenenitrile manuf isomerization cyclooctadienickel complex catalyst phosphonite ligand
 IT Hydrocyanation
 Hydrocyanation catalysts
 Isomerization
 Isomerization catalysts
 (group VIII metal complex catalyst with bidentate phosphonite ligand and manufacture of alkenenitriles)
 IT Group VIII elements
 RL: CAT (Catalyst use); USES (Uses)
 (group VIII metal complex catalyst with bidentate phosphonite ligand and manufacture of alkenenitriles)
 IT Nitriles, preparation
 RL: IMF (Industrial manufacture); PREP (Preparation)
 (unsatd., monoolefinic CS-; group VIII metal complex catalyst with bidentate phosphonite ligand and manufacture of alkenenitriles)
 IT 1295-35-8, Bis(1,5-Cyclooctadiene)nickel
 RL: CAT (Catalyst use); USES (Uses)
 (group VIII metal complex catalyst with bidentate phosphonite ligand and manufacture of alkenenitriles)
 IT 74-90-8, Hydrocyanic acid, reactions
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (hydrocyanation of butadiene; group VIII metal complex catalyst with bidentate phosphonite ligand and manufacture of alkenenitriles)
 IT 106-99-0, 1,3-Butadiene, reactions
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (hydrocyanation; group VIII metal complex catalyst with bidentate phosphonite ligand and manufacture of alkenenitriles)
 IT 252253-20-6 252253-21-7
 RL: CAT (Catalyst use); USES (Uses)
 (ligand; group VIII metal complex catalyst with bidentate phosphonite ligand and manufacture of alkenenitriles)
 IT 4635-87-4E, 3-Pentenenitrile 16529-56-9P, 2-Methyl-3-butenenitrile
 RL: IMF (Industrial manufacture); RCT (Reactant); PREP (Preparation); RACT (Reactant or reagent)
 (manufacture and isomerization; group VIII metal complex catalyst with bidentate phosphonite ligand and manufacture of alkenenitriles)
 IT 74-90-8, Hydrocyanic acid, reactions
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (hydrocyanation of butadiene; group VIII metal complex catalyst with bidentate phosphonite ligand and manufacture of alkenenitriles)
 RN 74-90-8 CAPLUS
 CN Hydrocyanic acid (CA INDEX NAME)

N
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IT 106-99-0, 1,3-Butadiene, reactions
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (hydrocyanation; group VIII metal complex catalyst with
 bidentate phosphonite ligand and manufacture of alkenenitriles)
 RN 106-99-0 CAPLUS
 CN 1,3-Butadiene (CA INDEX NAME)



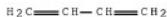
IT 4635-87-4P, 3-Pentenenitrile
 RL: IMF (Industrial manufacture); RCT (Reactant); PPEP
 (Preparation); RACT (Reactant or reagent)
 (manufacture and isomerization; group VIII metal complex catalyst
 with bidentate phosphonite ligand and manufacture of alkenenitriles)
 RN 4635-87-4 CAPLUS
 CN 3-Pentenenitrile (CA INDEX NAME)



L88 ANSWER 23 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN
 ACCESSION NUMBER: 1998:406229 CAPLUS Full-text
 DOCUMENT NUMBER: 129:82973
 TITLE: Monoolefinic C5 mononitrile production and use
 INVENTOR(S): Siegel, Wolfgang; Mundinger, Klaus; Meyer, Gerald;
 Fischer, Jakob
 PATENT ASSIGNEE(S): BASF A.-G., Germany
 SOURCE: Ger. Offen., 12 pp.
 CODEN: GWXXBX
 DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|---|------|----------|------------------|----------|
| DE 19652273 | A1 | 19980618 | DE 1996-19652273 | 19961216 |
| CA 2275164 | A1 | 19980625 | CA 1997-2275164 | 19971210 |
| WO 9827054 | A1 | 19980625 | WO 1997-EP6900 | 19971210 |
| W: AL, AU, BG, BR, BY, CA, CN, CZ, GE, HU, ID, IL, JP, KR, KZ, LT, LV, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TR, UA, US, AM, AZ, KG, MD, TJ, TM | | | | |
| RW: AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE AU 9858554 | A | 19980715 | AU 1998-58554 | 19971210 |

| | | | | |
|--|----|----------|------------------|------------|
| EP 944585 | A1 | 19990929 | EP 1997-954375 | 19971210 |
| EP 944585 | B1 | 20020417 | | |
| R: BE, DE, ES, FR, GB, IT, NL | | | | |
| CN 1245489 | A | 20000223 | CN 1997-181702 | 19971210 |
| CN 1144781 | B | 20040407 | | |
| BR 9713939 | A | 20000321 | BR 1997-13939 | 19971210 |
| JP 2001506250 | T | 20010515 | JP 1998-527270 | 19971210 |
| ES 2175520 | T3 | 20021116 | ES 1997-954375 | 19971210 |
| RU 2217416 | C2 | 20031127 | RU 1999-115156 | 19971210 |
| TW 387874 | B | 20000421 | TW 1997-86118914 | 19971215 |
| US 6197992 | B1 | 20010306 | US 1999-319877 | 19990614 |
| KR 2000057573 | A | 20000925 | KR 1999-705329 | 19990615 |
| PRIORITY APPLN. INFO.: | | | DE 1996-19652273 | A 19961216 |
| | | | WO 1997-EP6900 | W 19971210 |
| AB Non-conjugated C5 monoolefinic mononitriles are prepared economically by catalytic hydrocyanation of hydrocarbons containing butadiene (I) from which hydrocyanation poisons have been removed. The continuous reaction of a partially hydrogenated C4 fraction containing I (483 mmol/h) with HCN (414 mmol/h) in the presence of 2.76 mmol/h catalyst containing [(MeC6H4O)3P]4Ni 25, (MeC6H4O)3P 60, and 3-pentenenitrile (II)-2-methyl-3-butenenitrile (III) 15% at 102-95°/15 bar with residence time 80 min gave HCN conversion >99.8%, selectivity vs. I 98%, II-III ratio 2.0:1, and active Ni recovery 90.0%; vs. 98.0, 97, 1.95:1, and 61.3, resp., when a non-hydrogenated C4 fraction was used. | | | | |
| IC ICM C07C255-07 | | | | |
| ICS C07C253-10; C07C255-04; C07B035-02 | | | | |
| ICA B01J031-22 | | | | |
| CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes) Section cross-reference(s): 23 | | | | |
| IT 106-99-0, Butadiene, reactions RL: RCT (Reactant); RACT (Reactant or reagent) (hydrocyanation in purified C4 fractions) | | | | |
| IT 4635-97-4P, 3-Pentenenitrile 16529-56-9P, 2-Methyl-3-butenenitrile RL: IMF (Industrial manufacture); PREP (Preparation) (monoolefinic C5 mononitrile production and use) | | | | |
| IT 74-90-3, Hydrocyanic acid, reactions RL: FCT (Reactant); RACT (Reactant or reagent) (reaction with butadiene) | | | | |
| IT 106-99-0, Butadiene, reactions RL: RCT (Reactant); RACT (Reactant or reagent) (hydrocyanation in purified C4 fractions) | | | | |
| RN 106-99-0 CAPLUS | | | | |
| CN 1,3-Butadiene (CA INDEX NAME) | | | | |



IT 4635-87-4P, 3-Pentenenitrile
RL: IMF (Industrial manufacture); PREP (Preparation)
(monoolefinic C5 mononitrile production and use)
RN 4635-87-4 CAPLUS
CN 3-Pentenenitrile (CA INDEX NAME)



IT 74-90-8, Hydrocyanic acid, reactions
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (reaction with butadiene)
 RN 74-90-8 CAPLUS
 CN Hydrocyanic acid (CA INDEX NAME)



L88 ANSWER 24 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN
 ACCESSION NUMBER: 1997:679045 CAPLUS Full-text
 DOCUMENT NUMBER: 127:308629
 TITLE: Catalyzed vapor-phase hydrocyanation of diolefinic compounds
 INVENTOR(S): Druliner, Joe Douglas; Herron, Norman
 PATENT ASSIGNEE(S): E. I. Du Pont de Nemours & Co., USA; Druliner, Joe Douglas; Herron, Norman
 SOURCE: PCT Int. Appl., 19 pp.
 CODEN: PIXXD2
 DOCUMENT TYPE: Patent
 LANGUAGE: English
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|---|------|----------------|------------------|----------|
| WO 9736855 | A2 | 19971009 | WO 1997-US4903 | 19970327 |
| WO 9736855 | A3 | 19971106 | | |
| W: BR, CA, CN, JP, KR, SG, US, AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE | | | | |
| RW: AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE | | | | |
| IN 191521 | A1 | 20031206 | IN 1997-CA492 | 19970319 |
| TW 458959 | B | 20011011 | TW 1997-86103681 | 19970324 |
| EP 891323 | A2 | 19990120 | EP 1997-917016 | 19970327 |
| EP 891323 | B1 | 20060614 | | |
| R: DK, FR, GB, IT, NL | | | | |
| EP 1621531 | A1 | 20060201 | EP 2005-77325 | 19970327 |
| EP 1621531 | B1 | 20070314 | | |
| R: FR, GB, IT, NL | | | | |
| PRIORITY APPLN. INFO.: | | | | |
| | | US 1996-14618P | P 19960402 | |
| | | EP 1997-917016 | A3 19970327 | |
| | | WO 1997-US4903 | W 19970327 | |

OTHER SOURCE(S): MARPAT 127:308629
 AB A catalyzed vapor-phase process for the hydrocyanation of acyclic diolefinic compds. to olefinic nitriles comprises reacting an acyclic diolefinic compound with HCN in the vapor-phase at temperature 135-300° in the presence of a supported catalyst composition comprising at least one multidentate phosphite ligand, zero-valent nickel, and specially selected or treated supports.
 IC ICM C07C253-10
 CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)
 Section cross-reference(s): 23
 ST hydrocyanation diene vapor phase; catalyst hydrocyanation olefin nickel

10/586490

phosphite supported
IT Hydrocyanation
Hydrocyanation catalysts
(catalyzed vapor-phase hydrocyanation of diolefinic compds.)
IT 11063-09-5 180974-36-1
RL: CAT (Catalyst use); USES (Uses)
(catalyzed vapor-phase hydrocyanation of diolefinic compds.)
IT 169254-14-2P 169254-15-3P
RL: CAT (Catalyst use); IMF (Industrial manufacture); PREP (Preparation);
USES (Uses)
(catalyzed vapor-phase hydrocyanation of diolefinic compds.)
IT 592-51-8P, 4-Pentenenitrile 4635-87-4P, 3-Pentenenitrile
RL: IMF (Industrial manufacture); PREP (Preparation)
(catalyzed vapor-phase hydrocyanation of diolefinic compds.)
IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,
1,3-Butadiene, reactions 6108-61-8 108032-25-3, trans-2,4-Hexadiene
RL: RCT (Reactant); RACT (Reactant or reagent)
(catalyzed vapor-phase hydrocyanation of diolefinic compds.)
IT 9003-53-6, Polystyrene
RL: CAT (Catalyst use); USES (Uses)
(crosslinked, support; catalyzed vapor-phase hydrocyanation
of diolefinic compds.)
IT 7440-44-0, Carbon, uses
RL: CAT (Catalyst use); USES (Uses)
(heat-treated, support; catalyzed vapor-phase hydrocyanation
of diolefinic compds.)
IT 1344-28-1, Alumina, uses 7631-86-9, Silica, uses
9003-69-4, Divinylbenzene homopolymer 9058-15-5, Chromosorb 104
25014-41-9, Polyacrylonitrile
RL: CAT (Catalyst use); USES (Uses)
(support; catalyzed vapor-phase hydrocyanation of diolefinic
compds.)
IT 4635-87-4P, 3-Pentenenitrile
RL: IMF (Industrial manufacture); PREP (Preparation)
(catalyzed vapor-phase hydrocyanation of diolefinic compds.)
RN 4635-87-4 CAPLUS
CN 3-Pentenenitrile (CA INDEX NAME)



IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,
1,3-Butadiene, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(catalyzed vapor-phase hydrocyanation of diolefinic compds.)
RN 74-90-8 CAPLUS
CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 CAPLUS
CN 1,3-Butadiene (CA INDEX NAME)



IT 1344-28-1, Alumina, uses
 RL: CAT (Catalyst use); USES (Uses)
 (support; catalyzed vapor-phase hydrocyanation of diolefinic
 compds.)
 RN 1344-28-1 CAPLUS
 CN Aluminum oxide (Al2O3) (CA INDEX NAME)

*** STRUCTURE DIAGRAM IS NOT AVAILABLE ***

L88 ANSWER 25 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN
 ACCESSION NUMBER: 1991:412659 CAPLUS Full-text
 DOCUMENT NUMBER: 115:12659
 TITLE: Plasma discharge in nitrogen + methane at low
 pressures: experimental results and applications to
 Titan
 AUTHOR(S): Thompson, W. Reid; Henry, Todd J.; Schwartz, Joel M.;
 Khare, B. N.; Sagan, Carl
 CORPORATE SOURCE: Lab. Planet. Stud., Cornell Univ., Ithaca, NY, 14853,
 USA
 SOURCE: Icarus (1991), 90(1), 57-73
 CODEN: ICRSA5; ISSN: 0019-1035
 DOCUMENT TYPE: Journal
 LANGUAGE: English
 AB The yields of gaseous hydrocarbons and nitriles produced in a continuous flow,
 low-dose, cold plasma discharge excited in a 10% CH₄, 90% N₂ atmospheric at
 295 K and pressures (P) of 17 and 0.24 mbar are determined; the results are
 used to compute expected abundances of minor constituents in Titan's
 atmospheric These expts. are, by design, relevant to the atmospheric chemical
 induced by cosmic rays in Titan's troposphere and (at the lower P) to chemical
 initiated by Saturnian magnetospheric electrons and other charged particle
 sources which excite stratospheric auroras. At P = 17 mbar, 59 gaseous
 species including 27 nitriles are detected in overall yield 4.0 (C + N) atoms
 incorporated into products per 100 eV (heV). At P = 0.24 mbar, 19 species are
 detected, including 6 nitriles and 3 other unidentified N-bearing compds.; the
 yield is 0.79 (C + N)/heV, a mild decrease with P. The types of mols. formed
 change more markedly, with high degrees of multiple bonding at 0.24 mbar
 prevailing over more H-saturated mols. at 17 mbar. The mols. and yields at
 0.24 mbar bear a striking resemblance to the minor constituents found in
 Titan's atmospheric, all of which are abundant products in the laboratory
 experiment Using the altitude-integrated flux of charged particle energy
 deposition at Titan, the laboratory yields at P = 0.24 mbar, and a simple eddy
 mixing model, absolute stratospheric column abundances and mole fractions were
 computed. These are in very good agreement with the Voyager IRIS
 observations. Except for the primarily photochem. products, C₂H₆ and C₃H₈,
 the match is much better than that obtained by photochem.-kinetic models,
 demonstrating that properly designed laboratory expts. are directly applicable
 to modeling radiation-chemical processes in planetary atmospheres. On the
 basis of this agreement; CH₃-C.tplbond.N (ethanenitrile = acetonitrile)
 CH₂:CH-CH:CH₂ (1,3-butadiene), CH₂:C:CH₂ (1,2-propadiene = allene), and
 CH₂:CH-C.tplbond.CH (1-butene-3-yne) to be present at mol fractions X > 10⁻⁹,
 and CH₂:CH-C.tplbond.N (propenenitrile), CH₃-CH:CH₂ (propene), and CH₃-CH₂-
 C.tplbond.N (propanenitrile) at X > 10⁻¹⁰ are expected in Titan's atmospheric
 CC 53-9 (Mineralogical and Geological Chemistry)

- IT 74-84-0P, Ethane, preparation 74-85-1P, Ethene, preparation 74-86-2P,
 Ethyne, preparation 74-90-8P, Hydrocyanic acid, preparation
 74-98-6P, Propane, preparation 74-99-7P, 1-Propyne 75-05-8P,
 Ethanenitrile, preparation 75-19-4P, Cyclopropane 75-28-5P 75-83-2P,
 2,2-Dimethylbutane 78-78-4P, 2-Methylbutane 78-82-0P,
 2-Methylpropanenitrile 106-97-8P, Butane, preparation 106-98-9P,
 1-Butene, preparation 106-99-0P, 1,3-Butadiene, preparation
 107-00-6P, 1-Butyne 107-12-0P, Propanenitrile 107-13-1P,
 2-Propenenitrile, preparation 107-83-5P, 2-Methylpentane 109-66-0P,
 Pentane, preparation 109-67-1P, 1-Pentene 109-74-0P, Butanenitrile
 109-75-1P, 3-Butenenitrile 115-07-1P, Propene, preparation 115-11-7P,
 2-Methylpropene, preparation 126-98-7P, 2-Methyl-2-propenenitrile
 287-23-0P, Cyclobutane 290-96-0P, 1,2,4,5-Tetrazine 460-12-8P,
 1,3-Butadiyne 460-19-5P, Ethanenitrile 463-49-0P, Propadiene
 463-82-1P, 2,2-Dimethylpropane 503-17-3P, 2-Butyne 513-35-9P,
 2-Methyl-2-butene 542-92-7P, 1,3-Cyclopentadiene, preparation
 563-45-1P, 3-Methyl-1-butene 563-46-2P, 2-Methyl-1-butene 590-18-1P,
 cis-2-Butene 590-19-2P, 1,2-Butadiene 592-51-8P, 4-Pentenenitrile
 624-64-6P, trans-2-Butene 627-20-3P, cis-2-Pentene 627-26-9P,
 trans-2-Butenenitrile 630-18-2P, 2,2-Dimethylpropanenitrile 646-04-8P,
 trans-2-Pentene 689-97-4P, 1-Buten-3-yne 1070-71-9P, Propynenitrile
 1190-76-7P, cis-2-Butenenitrile 1516-01-4P, 2,4-Hexadienenitrile
 1615-70-9P, 2,4-Pentadienenitrile 4786-19-0P, 3-Methyl-3-butenenitrile
 5167-62-4P 13752-78-8P, 2-Butynenitrile 16529-56-9P,
 2-Methyl-3-butenenitrile 16529-66-1P, trans-3-Pentenenitrile
 17761-23-8P 20068-02-4P 25899-50-7P, cis-2-Pentenenitrile
 26294-98-4P, trans-2-Pentenenitrile 30574-97-1P
 RL: GFM (Geological or astronomical formation); FORM (Formation,
 nonpreparative); PREP (Preparation)
 (formation of, continuous flow plasma discharge irradiation of nitrogen-
 and methane-containing atmospheric in relation to)
 IT 74-82-8, Methane, occurrence 7727-37-9, Nitrogen, occurrence
 RL: OCCU (Occurrence)
 (in Titan's atmospheric, plasma discharge in, exptl. study in relation to)
 IT 74-90-8P, Hydrocyanic acid, preparation 106-99-0P,
 1,3-Butadiene, preparation 16529-66-1P, trans-3-Pentenenitrile
 RL: GFM (Geological or astronomical formation); FORM (Formation,
 nonpreparative); PREP (Preparation)
 (formation of, continuous flow plasma discharge irradiation of nitrogen-
 and methane-containing atmospheric in relation to)
 RN 74-90-8 CAPLUS
 CN Hydrocyanic acid (CA INDEX NAME)



- RN 106-99-0 CAPLUS
 CN 1,3-Butadiene (CA INDEX NAME)

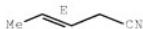


- RN 16529-66-1 CAPLUS

10/586490

CN 3-Pentenenitrile, (3E)- (CA INDEX NAME)

Double bond geometry as shown.



IT 7727-37-9, Nitrogen, occurrence

RL: OCCU (Occurrence)

(in Titan's atmospheric, plasma discharge in, exptl. study in relation to)

RN 7727-37-9 CAPLUS

CN Nitrogen (CA INDEX NAME)

~~H~~=N

L88 ANSWER 26 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 1984:50763 CAPLUS Full-text

DOCUMENT NUMBER: 100:50763

ORIGINAL REFERENCE NO.: 100:7757a,7760a

TITLE: Catalytic hydrocyanation of olefins by nickel(0)
phosphite complexes - effects of Lewis acids

AUTHOR(S): Tolman, C. A.; Seidel, W. C.; Druliner, J. D.;
Domaille, P. J.

CORPORATE SOURCE: Cent. Res. Dev. Dep., E. I. du Pont de Nemours and
Co., Wilmington, DE, 19898, USA

SOURCE: Organometallics (1984), 3(1), 33-8
CODEN: ORGND7; ISSN: 0276-7333

DOCUMENT TYPE: Journal
LANGUAGE: English

AB In this abstract L = (*o*-MeC₆H₄O)₃P (I) or (*p*-MeC₆H₄O)₃P (II). Mechanistic studies on the addition of HCN to olefins using Ni-3I catalyst show that the reactions proceed under mild conditions via (η^1 -organo)- or (η^3 -organo)nickel cyanide intermediates, formed by the insertion of monoenes or dienes into the Ni-H bond of L₃NiHCN. The RNiLmCN intermediates are identified by NMR and IR in some cases. In the case of very electroneg. R groups (formed for example from reactions of L₃NiHCN with C₂F₄ or CH₂:CHCN), reductive elimination does not occur, and the catalyst is poisoned for olefin hydrocyanation. Improved rates, catalyst lifetimes, and product linearity are obtained by the addition of Lewis acid (Q) cocatalysts. Spectroscopic studies show that Lewis acids coordinate strongly to the N atom lone-electron pair of hydrido cyanide intermediates to form L₃NiHCN⁺Q⁻. The effects of Lewis acids on hydrocyanation involves increasing the concentration of Ni in catalytic loop species (in the II system), accelerating the rate of C-C coupling to form alkenenitriles from alkylnickel cyanide complexes, and destabilizing relatively bulky branched alkyl intermediates relative to less crowded linear ones.

CC 22-4 (Physical Organic Chemistry)

Section cross-reference(s): 29

ST mechanism alkene hydrocyanation; kinetics alkene hydrocyanation; nickel phosphite complex hydrocyanation catalyst; Lewis acid hydrocyanation catalyst

IT Alkenes, reactions

- RL: RCT (Reactant); RACT (Reactant or reagent)
 (catalytic hydrocyanation of, Lewis acid effects and
 mechanism of)
- IT Lewis acids
 RL: PRP (Properties)
 (effect of, on hydrocyanation of alkenes catalyzed by nickel
 phosphite complexes)
- IT Hydrocyanation catalysts
 (nickel phosphite complexes, for alkenes, effect of Lewis acids in
 relation to mechanism with)
- IT Regiochemistry
 (of catalytic hydrocyanation of alkenes by nickel phosphite
 complexes)
- IT Steric effect
 Substituent effect
 (on catalytic hydrocyanation of alkenes)
- IT Addition reaction
 (oxidative, in catalytic hydrocyanation of alkenes)
- IT 960-71-4 1088-01-3 1095-03-0 7446-70-0, uses and miscellaneous
 7646-85-7, uses and miscellaneous 42270-57-5
 RL: PRP (Properties)
 (effect of, on nickel phosphite complex catalyzed
 hydrocyanation of olefins)
- IT 28829-00-7 87482-65-3
 RL: CAT (Catalyst use); USES (Uses)
 (hydrocyanation catalyst, for alkenes, mechanism with)
- IT 106-99-0, reactions 115-07-1, reactions
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (hydrocyanation of, mechanism of nickel phosphite catalyzed)
- IT 100-42-5, reactions 558-37-2 592-42-7 592-48-3 592-51-8
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (hydrocyanation of, mechanism of nickel phosphite complex
 catalyzed)
- IT 107-12-0P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (preparation of, from hydrocyanation of ethylene, mechanism of
 catalytic)
- IT 87482-64-2P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (preparation of, in catalytic hydrocyanation of hexadienes)
- IT 17611-82-4P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (preparation of, in catalytic hydrocyanation of pentenenitrile)
- IT 4635-87-4P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (preparation, double bond isomerization, and hydrocyanation of, mechanism
 of)
- IT 74-90-8, reactions
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (reaction of, with nickel phosphite complex)
- IT 106-99-0, reactions
 RL: RCT (Reactant); PACT (Reactant or reagent)
 (hydrocyanation of, mechanism of nickel phosphite catalyzed)
- RN 106-99-0 CAPLUS
- CN 1,3-Butadiene (CA INDEX NAME)



IT 4635-8/-4P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (preparation, double bond isomerization, and hydrocyanation of, mechanism
 of)
 RN 4635-87-4 CAPLUS
 CN 3-Pentenenitrile (CA INDEX NAME)



IT 74-90-8, reactions
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (reaction of, with nickel phosphite complex)
 RN 74-90-8 CAPLUS
 CN Hydrocyanic acid (CA INDEX NAME)



L88 ANSWER 27 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN
 ACCESSION NUMBER: 1984:490011 CAPLUS Full-text
 DOCUMENT NUMBER: 101:90011
 ORIGINAL REFERENCE NO.: 101:13795a,13798a
 TITLE: Homogeneous nickel-catalyzed olefin hydrocyanation
 AUTHOR(S): Seidel, W. C.; Tolman, C. A.
 CORPORATE SOURCE: E. I. du Pont de Nemours and Co., Wilmington, DE,
 19898, USA
 SOURCE: Annals of the New York Academy of Sciences (1983),
 415(Catal. Transition Met. Hydrides), 201-21
 CODEN: ANYAA9; ISSN: 0077-8923
 DOCUMENT TYPE: Journal
 LANGUAGE: English
 AB Olefin hydrocyanation follows the 16- and 18-electron rule. Activated olefins like CH₂:CH₂ or CH₂:CHCH:CH₂ add HCN without Lewis acids at high rates to give good yields of nitriles. Unactivated olefins (e.g., 4-pentenenitrile) require both Lewis acids and Ni(0) complexes for efficient linear hydrocyanation. The kinetics and mechanisms of these reactions are discussed.
 CC 22-4 (Physical Organic Chemistry)
 ST hydrocyanation alkene kinetics mechanism; nickel hydrocyanation catalyst homogeneous
 IT Alkenes, reactions
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (hydrocyanation of, kinetics and mechanism of homogeneous nickel
 catalyzed)
 IT Hydrocyanation catalysts
 (nickel phosphines, for alkenes, kinetics and mechanism with)
 IT Kinetics of hydrocyanation
 (of alkenes in presence of nickel-phosphine catalyst)
 IT 960-71-4 1088-01-3 1095-03-0 42270-57-5
 RL: RCT (Reactant); RACT (Reactant or reagent)

(effect of, on nickel-phosphine complex catalyzed hydrocyanation of olefins)

IT 74-90-8, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)
(hydrocyanation by, nickel phosphine complexes as catalysts for)

IT 74-85-1, reactions 107-13-1, reactions 109-75-1 592-41-6, reactions 592-51-8 5048-19-1 16529-66-1 25899-50-7 26294-98-4

RL: RCT (Reactant); RACT (Reactant or reagent)
(hydrocyanation of, equilibrium for nickel complex catalyzed)

IT 106-99-0, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)
(hydrocyanation of, mechanism of nickel complex catalyzed)

IT 4635-87-4P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP
(Preparation); RACT (Reactant or reagent)
(preparation and hydrocyanation of)

IT 74-90-8, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)
(hydrocyanation by, nickel phosphine complexes as catalysts for)

RN 74-90-8 CAPLUS

CN Hydrocyanic acid (CA INDEX NAME)



IT 106-99-0, reactions

RL: PCT (Reactant); PACT (Reactant or reagent)
(hydrocyanation of, mechanism of nickel complex catalyzed)

RN 106-99-0 CAPLUS

CN 1,3-Butadiene (CA INDEX NAME)



IT 4635-87-4P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP
(Preparation); RACT (Reactant or reagent)
(preparation and hydrocyanation of)

RN 4635-87-4 CAPLUS

CN 3-Pentenenitrile (CA INDEX NAME)



DOCUMENT NUMBER: 83:58183
 ORIGINAL REFERENCE NO.: 83:9163a,9166a
 TITLE: Organic nitriles
 INVENTOR(S): Waddan, Dhafer Y.; Crooks, Graham R.
 PATENT ASSIGNEE(S): Imperial Chemical Industries Ltd., UK
 SOURCE: Ger. Offen., 17 pp.
 CODEN: GWXXBX
 DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------------------------|------|----------|-----------------|------------|
| DE 2450863 | A1 | 19750507 | DE 1974-2450863 | 19741025 |
| GB 1482909 | A | 19770817 | GB 1973-50604 | 19741007 |
| US 3947487 | A | 19760330 | US 1974-514315 | 19741011 |
| BE 821270 | A1 | 19750418 | BE 1974-149706 | 19741018 |
| JP 50071626 | A | 19750613 | JP 1974-124213 | 19741028 |
| JP 58002231 | B | 19830114 | | |
| NL 7414172 | A | 19750502 | NL 1974-14172 | 19741030 |
| FR 2249874 | A1 | 19750530 | FR 1974-36272 | 19741030 |
| PRIORITY APPLN. INFO.: | | | GB 1973-50604 | A 19731031 |
| | | | GB 1974-2194 | A 19740117 |

AB Organic sulfides [e.g., Pr₂S, (PhCH₂)₂S] and CuCl or CuBr were used as catalysts for addition of HCN to butadiene or isoprene. Thus, heating 19.5 g butadiene, 15 ml HCN, and 1.8 g CuCl in 3 ml thiophene 17 hr at 120° (sealed tube) gave 91.6% 3-pentenenitrile and 8.4% 2-methyl-3-butenenitrile.

IC C07C

CC 23-19 (Aliphatic Compounds)

ST addn hydrocyanic acid diene catalyst; olefinic aliph nitrile; butadiene hydrocyanic acid addn catalyst; isoprene hydrocyanic acid addn catalyst

IT Addition reaction catalysts

(cuprous halides-organic sulfides for butadiene and isoprene with hydrocyanic acid)

IT 74-90-8

RL: PCT (Reactant); PACT (Reactant or reagent)

(addition reaction of, with butadiene and isoprene, catalysts for)

IT 78-79-5, reactions 106-99-0, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)

(addition reaction of, with hydrocyanic acid, catalysts for)

IT 75-18-3 108-98-5 110-02-1 111-48-8 139-66-2 352-93-2 544-02-5
7787-70-4

RL: CAT (Catalyst use); USES (Uses)

(catalysts, for addition reaction of butadiene with hydrocyanic acid)

IT 111-47-7 538-74-9 7758-89-6

RL: CAT (Catalyst use); USES (Uses)

(catalysts, for addition reaction of hydrocyanic acid with butadiene and isoprene)

IT 4635-87-4P 16529-56-9P

RL: PREP (Preparation)

(from butadiene by reaction with hydrocyanic acid, catalysts for)

IT 4786-23-6P

RL: PREP (Preparation)

(from isoprene by reaction with hydrocyanic acid, catalysts for)

IT 74-90-8

10/586490

RL: RCT (Reactant); RACT (Reactant or reagent)
(addition reaction of, with butadiene and isoprene, catalysts
for)

RN 74-90-8 CAPLUS

CN Hydrocyanic acid (CA INDEX NAME)



IT 106-99-0, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)
(addition reaction of, with hydrocyanic acid, catalysts for)

RN 106-99-0 CAPLUS

CN 1,3-Butadiene (CA INDEX NAME)



IT 4635-87-4P

RL: PREP (Preparation)
(from butadiene by reaction with hydrocyanic acid, catalysts
for)

RN 4635-87-4 CAPLUS

CN 3-Pentenenitrile (CA INDEX NAME)



L88 ANSWER 29 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 1975:97704 CAPLUS Full-text

DOCUMENT NUMBER: 82:97704

ORIGINAL REFERENCE NO.: 82:15593a,15596a

TITLE: Hydrocyanation of conjugated diolefins
INVENTOR(S): Seidel, William C.; Tolman, Chadwick A.

PATENT ASSIGNEE(S): du Pont de Nemours, E. I., and Co.

SOURCE: U.S., 3 pp.

CODEN: USXXAM

DOCUMENT TYPE: Patent

LANGUAGE: English

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------------|------|----------|-----------------|----------|
| US 3850973 | A | 19741126 | US 1973-401072 | 19730926 |
| BE 820308 | A1 | 19750325 | BE 1974-148862 | 19740925 |
| DE 2445731 | A1 | 19750403 | DE 1974-2445731 | 19740925 |
| FR 2244753 | A1 | 19750418 | FR 1974-32324 | 19740925 |

FR 2244753 B1 19790202
 JP 50059326 A 19750522 JP 1974-109629 19740925
 JP 58042183 B 19830917
 GB 1436932 A 19760526 GB 1974-41704 19740925
 PRIORITY APPLN. INFO.: US 1973-401072 A 19730926
 AB HCN reacted with H₂C:CHCH:CH₂ at -50 to +150° in the presence of Ni[P-(OC₆H₄Me-4)]₃(NCCH₂CH:CHMe)₃ to give a 2:1 mixture of NCCH₂CH:CHMe and NCCHMeCH:CH₂.
 IC C07C
 INCL 260464000
 CC 23-19 (Aliphatic Compounds)
 IT Hydrocyanation catalysts
 (nickel π -allyl complexes, for dienes)
 IT 54637-55-7 54637-56-8
 RL: CAT (Catalyst use); USES (Uses)
 (catalysts, for diene hydrocyanation)
 IT 106-99-0, reactions 542-92-7
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (hydrocyanation of, catalysts for)
 IT 3047-38-9P 4492-41-5P 4635-87-4P 16529-56-9P 26555-56-6P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (preparation of)
 IT 74-90-8
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (reaction of, with dienes)
 IT 106-99-0, reactions
 RL: PCT (Reactant); RACT (Reactant or reagent)
 (hydrocyanation of, catalysts for)
 RN 106-99-0 CAPLUS
 CN 1,3-Butadiene (CA INDEX NAME)



IT 4635-87-4P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (preparation of)
 RN 4635-87-4 CAPLUS
 CN 3-Pentenenitrile (CA INDEX NAME)



IT 74-90-8
 RL: PCT (Reactant); RACT (Reactant or reagent)
 (reaction of, with dienes)
 RN 74-90-8 CAPLUS
 CN Hydrocyanic acid (CA INDEX NAME)



L88 ANSWER 30 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN
 ACCESSION NUMBER: 1974:145481 CAPLUS Full-text
 DOCUMENT NUMBER: 80:145481
 ORIGINAL REFERENCE NO.: 80:23477a,23480a
 TITLE: 3-Pentenenitrile
 INVENTOR(S): Waddan, Dhafir Y.
 PATENT ASSIGNEE(S): Imperial Chemical Industries Ltd.
 SOURCE: Ger. Offen., 11 pp.
 CODEN: GWXXBX
 DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------------------------|---|---------------|-----------------|----------|
| DE 2344767 | A1 | 19740314 | DE 1973-2344767 | 19730905 |
| GB 1429169 | A | 19760324 | GB 1972-41487 | 19730821 |
| US 3869501 | A | 19750304 | US 1973-392008 | 19730827 |
| BE 804557 | A1 | 19740306 | BE 1973-135401 | 19730906 |
| FR 2198932 | A1 | 19740405 | FR 1973-32127 | 19730906 |
| IT 998546 | B | 19760220 | IT 1973-28647 | 19730906 |
| JP 49092022 | A | 19740903 | JP 1973-100388 | 19730907 |
| PRIORITY APPLN. INFO.: | | GB 1972-41487 | A | 19720907 |
| AB | MeCH:CHCH ₂ CN was prepared in ≤88.8% yield by reaction of CH ₂ :CHCH:CH ₂ with HCN in the presence of CuCl in organic acids, e.g. AcOH. | | | |
| IC | C07C | | | |
| CC | 23-19 (Aliphatic Compounds) | | | |
| ST | pentenenitrile; copper chloride catalyst | | | |
| IT | Addition reaction catalysts (copper chloride, for hydrocyanic acid to butadiene) | | | |
| IT | 7758-89-6 | | | |
| RL | CAT (Catalyst use); USES (Uses) (catalysts, in hydrocyanic acid addition to butadiene) | | | |
| IT | 4635-87-4P | | | |
| RL | SPN (Synthetic preparation); PREP (Preparation) (preparation of) | | | |
| IT | 74-90-8 | | | |
| RL | RCT (Reactant); RACT (Reactant or reagent) (reaction of, with butadiene) | | | |
| IT | 106-39-0, reactions | | | |
| RL | RCT (Reactant); RACT (Reactant or reagent) (with hydrocyanic acid) | | | |
| IT | 4635-87-4P | | | |
| RL | SPN (Synthetic preparation); PREP (Preparation) (preparation of) | | | |
| RN | 4635-87-4 CAPLUS | | | |
| CN | 3-Pentenenitrile (CA INDEX NAME) | | | |



RL: RCT (Reactant); RACT (Reactant or reagent)
 (reaction of, with butadiene)
 RN 74-90-8 CAPLUS
 CN Hydrocyanic acid (CA INDEX NAME)



IT 106-99-0, reactions
 RL: RCT (Reactant); PACT (Reactant or reagent)
 (with hydrocyanic acid)
 RN 106-99-0 CAPLUS
 CN 1,3-Butadiene (CA INDEX NAME)



L88 ANSWER 31 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN
 ACCESSION NUMBER: 1974:120342 CAPLUS Full-text
 DOCUMENT NUMBER: 80:120342
 ORIGINAL REFERENCE NO.: 80:19367a,19370a
 TITLE: 3-Pentenenitrile
 INVENTOR(S): Waddan, Dhafir Y.
 PATENT ASSIGNEE(S): Imperial Chemical Industries Ltd.
 SOURCE: Ger. Offen., 13 pp.
 CODEN: GWXXBX
 DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|-------------|------|----------|-----------------|----------|
| DE 2336852 | A1 | 19740214 | DE 1973-2336852 | 19730719 |
| DE 2336852 | C2 | 19841004 | | |
| GB 1429651 | A | 19760324 | GB 1972-35639 | 19730705 |
| US 3849472 | A | 19741119 | US 1973-377183 | 19730709 |
| BE 802730 | A1 | 19740124 | BE 1973-133817 | 19730724 |
| IT 995062 | B | 19751110 | IT 1973-27010 | 19730724 |
| NL 7310509 | A | 19740204 | NL 1973-10509 | 19730730 |
| FR 2194691 | A1 | 19740301 | FR 1973-27817 | 19730730 |
| JP 49092020 | A | 19740903 | JP 1973-85514 | 19730731 |
| JP 57026267 | B | 19820603 | | |

PRIORITY APPLN. INFO.: GB 1972-35639 A 19720731

AB 3-Pentenenitrile (I), useful for the manufacture of adiponitrile, was prepared by reaction of CH₂:CHCH:CH₂ (II) with HCN in the presence of a complex of CuCl with an organic nitrile, e.g. (NC)2C:C(CN)₂ (III) and MeCN. Thus, II and HCN were added to CuCl, III, and MeCN at -20° and the mixture heated 60 hr at 100° in a closed vessel to give 88.3% I.

IC C07C

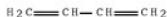
CC 23-19 (Aliphatic Compounds)

10/586490

ST pentenenitrile; butadiene hydrocyanation catalyst; copper complex hydrocyanation catalyst; nitrile complex hydrocyanation catalyst
IT Nitriles, uses and miscellaneous
RL: CAT (Catalyst use); USES (Uses)
(catalysts, with cuprous chloride, for hydrocyanation of butadiene)
IT Hydrocyanation catalysts
(cuprous chloride, containing organic nitriles, for butadiene)
IT 4635-87-4P
RL: PPEP (Preparation)
(by hydrocyanation of butadiene)
IT 75-05-8, uses and miscellaneous 107-13-1, uses and miscellaneous 670-54-2, uses and miscellaneous
RL: CAT (Catalyst use); USES (Uses)
(catalysts, containing cuprous chloride, for hydrocyanation of butadiene)
IT 7758-89-6
RL: CAT (Catalyst use); USES (Uses)
(catalysts, containing organic nitriles, for hydrocyanation of butadiene)
IT 106-99-0, reactions
RL: PCT (Reactant); PACT (Reactant or reagent)
(hydrocyanation of, catalysts for)
IT 74-90-8
RL: RCT (Reactant); RACT (Reactant or reagent)
(reaction of, with butadiene, catalysts for)
IT 4635-87-4P
RL: PPEP (Preparation)
(by hydrocyanation of butadiene)
RN 4635-87-4 CAPLUS
CN 3-Pentenenitrile (CA INDEX NAME)



IT 106-99-0, reactions
RL: PCT (Reactant); PACT (Reactant or reagent)
(hydrocyanation of, catalysts for)
RN 106-99-0 CAPLUS
CN 1,3-Butadiene (CA INDEX NAME)



IT 74-90-8
RL: RCT (Reactant); RACT (Reactant or reagent)
(reaction of, with butadiene, catalysts for)
RN 74-90-8 CAPLUS
CN Hydrocyanic acid (CA INDEX NAME)



L88 ANSWER 32 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN
 ACCESSION NUMBER: 1973:135702 CAPLUS Full-text
 DOCUMENT NUMBER: 78:135702
 ORIGINAL REFERENCE NO.: 78:21789a,21792a
 TITLE: Unsaturated nitriles
 INVENTOR(S): Albanese, Pietro; Bennoni, Luigi; Carnisio, Giuseppe;
 Colombo, Luigi
 PATENT ASSIGNEE(S): Montecatini Edison S.p.A.
 SOURCE: Ital., 10 pp.
 CODEN: ITXXAX
 DOCUMENT TYPE: Patent
 LANGUAGE: Italian
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------------|--|----------|-----------------|----------|
| IT 869902 | ----- | 19700819 | IT | 19690812 |
| AB | Butacience reacts with HCN in the presence of Fe(CO)5-Ph2P(CH2) PPh2 reaction products (n = 0-12) to give CH2:CHCHMeCN, MeCH:CHCH2CN, trans-MeCH:CMcCN, and 3-vinylcyclohexene. The diphosphine-Fe(CO)5 molar ratio is 1-10:1. | | | |
| IC | C07C | | | |
| CC | 23-19 (Aliphatic Compounds) | | | |
| ST | budadiene addn hydrogen cyanide; iron carbonyl addn reaction catalyst; diphosphine deriv addn reaction catalyst; pentenonitrile prepn; butenonitrile methyl; methylbutenonitrile prepn | | | |
| IT | Addition reaction catalysts (diphosphine-iron pentacarbonyl complexes, for butadiene with hydrocyanic acid) | | | |
| IT | 74-90-8 RL: RCT (Reactant); RACT (Reactant or reagent) (addition reaction with butadiene, catalysts for) | | | |
| IT | 106-99-0, reactions RL: RCT (Reactant); RACT (Reactant or reagent) (addition reaction with hydrocyanic acid, catalysts for) | | | |
| IT | 1101-41-3 7688-25-7 19845-69-3 27721-02-4 27721-03-5 41625-30-3 41625-32-5 RL: CAT (Catalyst use); USES (Uses) (catalyst, for addition of hydrocyanic acid to butadiene) | | | |
| IT | 766-03-0P 4635-87-4P 16529-56-9P 30574-97-1P RL: SPN (Synthetic preparation); PREP (Preparation) (preparation of) | | | |
| IT | 74-90-8 RL: RCT (Reactant); RACT (Reactant or reagent) (addition reaction with butadiene, catalysts for) | | | |
| RN | 74-90-8 CAPLUS | | | |
| CN | Hydrocyanic acid (CA INDEX NAME) | | | |



IT 106-99-0, reactions
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (addition reaction with hydrocyanic acid, catalysts for)
 RN 106-99-0 CAPLUS
 CN 1,3-Butadiene (CA INDEX NAME)



IT 4635-87-4P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (preparation of)
 RN 4635-87-4 CAPLUS
 CN 3-Pentenenitrile (CA INDEX NAME)



L88 ANSWER 33 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN
 ACCESSION NUMBER: 1973:135701 CAPLUS Full-text
 DOCUMENT NUMBER: 78:135701
 ORIGINAL REFERENCE NO.: 78:21789a,21792a
 TITLE: Unsaturated nitriles
 INVENTOR(S): Albanese, Pietro; Benzoni, Luigi; Carnisio, Giuseppe;
 Crivelli, Armando
 PATENT ASSIGNEE(S): Montecatini Edison S.p.A.
 SOURCE: Ital., 15 pp.
 CODEN: ITXXAX
 DOCUMENT TYPE: Patent
 LANGUAGE: Italian
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------------|------|----------|-----------------|----------|
| ----- | ---- | ----- | ----- | ----- |
| IT 869900 | | 19700819 | IT | 19690812 |

AB Mixts. of $\text{CH}_2:\text{CHCHMeCN}$, $\text{MeCH}:\text{CHCH}_2\text{CN}$, $\text{EtCH}:\text{CHCN}$, and cis- and trans- MeCH:CMcN are obtained by the addition of HCN to butadiene in the presence of reaction products of $\text{Ni}(\text{CO})_4$ and $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ (I) (n is an integer of 0-12). The I- $\text{Ni}(\text{CO})_4$ molar ratio is 1:1-10:1, the HCN- $\text{Ni}(\text{CO})_4$ molar ratio is 10:1-100:1, and the reaction temperature is 50-200°.

IC C07C

CC 23-19 (Aliphatic Compounds)

ST butadiene hydrogen cyanide addn; addn reaction catalyst diphosphine; diphosphine nickel carbonyl catalyst; pentenenitrile prepn; methylbutenenitrile prepn; butenenitrile methyl

IT Addition reaction catalysts

(diphosphine-nickel tetracarbonyl reaction products, for hydrocyanic acid with butadiene)

IT '74-90-8

RL: RCT (Reactant); PACT (Reactant or reagent)

(addition reaction with butadiene, catalysts for)
 IT 106-99-0, reactions
 RL: PCT (Reactant); RACT (Reactant or reagent)
 (addition reaction with hydrocyanic acid, catalysts for)
 IT 1663-45-2D, Phosphine, 1,2-ethanediylbis[diphenyl-, nickel complexes
 2071-20-7D, Phosphine, methylenebis[diphenyl-, nickel complexes
 6737-42-4D, Phosphine, 1,3-propanediylbis[diphenyl-, nickel complexes
 7688-25-7D, Phosphine, 1,4-butanediylbis[diphenyl-, nickel complexes
 RL: CAT (Catalyst use); USES (Uses)
 (catalyst, for addition reaction of hydrocyanic acid with
 butadiene)
 IT 1101-41-3D, Diphosphine, tetraphenyl-, nickel complexes 19845-69-3D,
 Phosphine, 1,6-hexanediylbis[diphenyl-, nickel complexes 27721-02-4D,
 Phosphine, 1,5-pentanediylbis[diphenyl-, nickel complexes 27721-03-5D,
 Phosphine, 1,10-decanediylbis[diphenyl-, nickel complexes 41625-30-3D,
 Phosphine, 1,8-octanediylbis[diphenyl-, nickel complexes 41625-32-5D,
 Phosphine, 1,12-dodecanediylbis[diphenyl-, nickel complexes
 RL: CAT (Catalyst use); USES (Uses)
 (catalyst, for hydrocyanic acid addition reaction with
 butadiene)
 IT 4635-87-4P 16529-56-9P 16529-66-1P 20068-02-4P
 25899-50-7P 30574-97-1P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (preparation of)
 IT 74-90-8
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (addition reaction with butadiene, catalysts for)
 RN 74-90-8 CAPLUS
 CN Hydrocyanic acid (CA INDEX NAME)



IT 106-99-0, reactions
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (addition reaction with hydrocyanic acid, catalysts for)
 RN 106-99-0 CAPLUS
 CN 1,3-Butadiene (CA INDEX NAME)



IT 4635-87-4P 16529-66-1P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (preparation of)
 RN 4635-87-4 CAPLUS
 CN 3-Pentenenitrile (CA INDEX NAME)



RN 16529-66-1 CAPLUS
 CN 3-Pentenenitrile, (3E)- (CA INDEX NAME)

Double bond geometry as shown.



L88 ANSWER 34 OF 60 CAPLUS COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 1949:22671 CAPLUS Full-text
 DOCUMENT NUMBER: 43:22671
 ORIGINAL REFERENCE NO.: 43:4286b-c
 TITLE: Unsaturated nitriles
 INVENTOR(S): Schulze, Walter A.; Mahan, John E.
 PATENT ASSIGNEE(S): Phillips Petroleum Co.
 DOCUMENT TYPE: Patent
 LANGUAGE: Unavailable
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------------|--|----------|-----------------|----------|
| US 2464723 | ----- | 19490315 | US 1944-563744 | 19441116 |
| AB | A liquid stream of a conjugated diolefin and HCN in a mol. ratio between 2:1 and 1.25:1, with MeCN as a diluent, is passed over a solid porous anhydrous CuCl catalyst at 100-350°F. and at a pressure of 100-700 lb./sq. in. An unsatd. nitrile is recovered from the effluent stream; e.g., butadiene and HCN give 36% conversion of pentenenitrile. | | | |
| CC | 10 (Organic Chemistry) | | | |
| IT | 4635-87-4P, 3-Pentenenitrile | | | |
| | RL: PREP (Preparation) (preparation of) | | | |
| IT | 74-90-8, Hydrocyanic acid (reaction with diolefins) | | | |
| IT | 106-99-0, 1,3-Butadiene (reactions of, with HCN) | | | |
| IT | 4635-87-4P, 3-Pentenenitrile | | | |
| | RL: PREP (Preparation) (preparation of) | | | |
| RN | 4635-87-4 CAPLUS | | | |
| CN | 3-Pentenenitrile (CA INDEX NAME) | | | |



IT 74-90-8, Hydrocyanic acid
 (reaction with diolefins)
 RN 74-90-8 CAPLUS
 CN Hydrocyanic acid (CA INDEX NAME)

N
H

IT 106-99-0, 1,3-Butadiene
(reactions of, with HCN)
RN 106-99-0 CAPLUS
CN 1,3-Butadiene (CA INDEX NAME)



L88 ANSWER 35 OF 60 CASREACT COPYRIGHT 2008 ACS on STN
 ACCESSION NUMBER: 138:304408 CASREACT Full-text
 TITLE: Use of chelating phosphonites with transition metals
 as catalysts
 INVENTOR(S): Bartsch, Michael; Baumann, Robert; Kunsmann-keitel,
 Dagmar Pasca; Haderlein, Gerd; Jungkamp, Tim;
 Altmaier, Marco; Siegel, Wolfgang; Molnar, Ferenc
 BASF AG, Germany
 SOURCE: Ger. Offen., 14 pp.
 CODEN: GWXXBX
 DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|---|------|----------|------------------|----------|
| DE 10150286 | A1 | 20030417 | DE 2001-10150286 | 20011012 |
| CA 2462720 | A1 | 20030424 | CA 2002-2462720 | 20021004 |
| WO 2003033142 | A1 | 20030424 | WO 2002-EP11108 | 20021004 |
| W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG | | | | |
| AU 2002362816 | A1 | 20030428 | AU 2002-362816 | 20021004 |
| EP 1438133 | A1 | 20040721 | EP 2002-801309 | 20021004 |
| R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, SK | | | | |
| BR 2002013108 | A | 20040921 | BR 2002-13108 | 20021004 |
| CN 1568225 | A | 20050119 | CN 2002-820102 | 20021004 |
| JP 2005505611 | T | 20050224 | JP 2003-535929 | 20021004 |

10/586490

MX 2004PA02764 A 20040629 MX 2004-PA2764 20040324
 US 2005090677 A1 20050428 US 2004-491911 20040408
 IN 2004CN1013 A 20060203 IN 2004-CN1013 20040511
PRIORITY APPLN. INFO.: DE 2001-10150286 20011012
 WO 2002-EP11108 20021004

OTHER SOURCE(S): MARPAT 138:304408
GI

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFF-LINE PRINT *

AB Phosphonites I, II, and III ($R_1, R_2, R_4 = \text{independently H, alkyl, C1-8 alkenyl, C1-8 alkoxy, } R_3 = \text{H, Me, X = F, Cl, CF}_3, n = 0-2$) are useful as ligands for nickel(0) catalyzed reactions. Thus, nickel(0)-(m-/p-tolylphosphite) catalyzed isomerization of 2-methyl-3-butenenitrile at 115° in 180 min gave 3-pentenenitrile which in presence of same catalyst, ZnCl_2 additive and HCN gave hydrocyanation product, adiponitrile.

BX(1) OF 5 A + B ==> C



RX(1) RCT A 106-99-0, B 74-90-8
 PRO C 4635-87-4
 CAT 1295-35-8 Ni dicyclooctadiene, 179259-60-0 Phosphinous acid,
 diphenyl-, [1,1'-biphenyl]-2,2'-diyl ester
 SOL 7732-18-5 Water, 109-99-9 THF
 CON 180 minutes, 25 - 80 deg C

L88 ANSWER 36 OF 60 CASREACT COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 138:30407 CASREACT Full-text
TITLE: Use of chelating phosphonites with transition metals
as catalysts
INVENTOR(S): Bartsch, Michael; Baumann, Robert; Kunsmann-keitel,
Dagmar Pasca; Haderlein, Gerd; Jungkamp, Tim;
Altmayer, Marco; Siegel, Wolfgang; Molnar, Ferenc
PATENT ASSIGNEE(S): BASF AG, Germany
SOURCE: Ger. Offen., 14 pp.
CODEN: GWXXBX
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

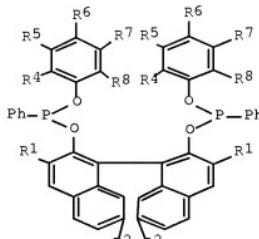
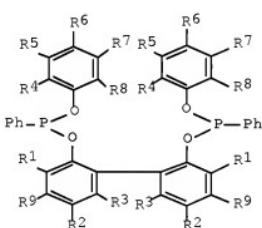
| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|-------------|------|----------|------------------|----------|
| DE 10150285 | A1 | 20030417 | DE 2001-10150285 | 20011012 |
| CA 2462719 | A1 | 20030424 | CA 2002-2462719 | 20021001 |

| | | | | |
|--|----|----------|------------------|----------|
| WO 2003033141 | A1 | 20030424 | WO 2002-EP10985 | 20021001 |
| W: AB, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW | | | | |
| RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG | | | | |
| AU 2002362813 | A1 | 20030428 | AU 2002-362813 | 20021001 |
| EP 1438132 | A1 | 20040721 | EP 2002-801302 | 20021001 |
| EP 1438132 | B1 | 20070425 | | |
| R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, SK | | | | |
| BR 2002012966 | A | 20041013 | BR 2002-12966 | 20021001 |
| CN 1568226 | A | 20050119 | CN 2002-820103 | 20021001 |
| JP 2005050610 | T | 20050224 | JP 2003-535928 | 20021001 |
| AT 360481 | T | 20070515 | AT 2002-801302 | 20021001 |
| ES 2284977 | T3 | 20071116 | ES 2002-2801302 | 20021001 |
| MX 2004PA02437 | A | 20040629 | MX 2004-PA2437 | 20040315 |
| US 2004235648 | A1 | 20041125 | US 2004-491964 | 20040408 |
| US 7022866 | B2 | 20060404 | | |
| IN 2004CN01014 | A | 20060203 | IN 2004-CN1014 | 20040511 |
| PRIORITY APPLN. INFO.: | | | DE 2001-10150285 | 20011012 |
| | | | WO 2002-EP10985 | 20021001 |

OTHER SOURCE(S):

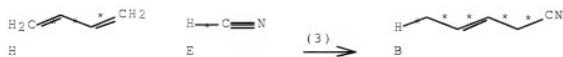
MARPAT 138:304407

GI



AB Phosphonites I and II ($R_1, R_2 = \text{independently } H, \text{ alkyl, C1-8 alkenyl, C1-8 alkoxy}$, $R_3 = H, Me, R_4 = \text{tert-Bu}$, $R_5, R_6, R_7, R_8, R_9 = H, \text{ alkyl, C1-8 alkenyl}$) are useful as ligands for nickel(0) catalyzed reactions. Thus, nickel(0)-(m-/p-tolylphosphite) catalyzed isomerization of 2-methyl-3-butenenitrile at 115° in 180 min gave 3-pentenenitrile which in presence of same catalyst, ZnCl₂ additive and HCN gave hydrocyanation product, adipodinitrile.

RX(3) OF 5 H + E ==> B...



RX(3) RCT H 106-99-0, E 74-90-8
 PRO B 4635-87-4
 CAT 125280-25-3 Nickel, tetrakis[tris(3(or 4)-methylphenyl)
 phosphite-κP]-
 SOL 7732-18-5 Water, 109-99-9 THF
 CON 180 minutes, 25 - 80 deg C

L88 ANSWER 37 OF 60 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 125:195996 CASREACT Full-text
 TITLE: Hydrocyanation of diolefins and isomerization of nonconjugated 2-alkyl-3-monoalkenenitriles in liquid phase in presence of zero-valent nickel and multidentate phosphite ligands and preparation of phosphorochloridites and diaryl N,N-dialkylphosphoramidites

INVENTOR(S): Foo, Thomas; Garner, James Michael; Shapiro, Rafael; Tam, Wilson

PATENT ASSIGNEE(S): E. I. Du Pont de Nemours & Co., USA
 SOURCE: PCT Int. Appl., 90 pp.

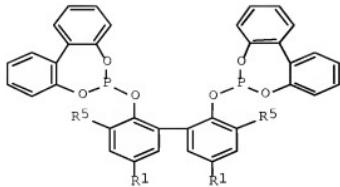
DOCUMENT TYPE: Patent

LANGUAGE: English

FAMILY ACC. NUM. COUNT: 2

PATENT INFORMATION:

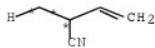
| PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|--|-------------------|----------|-----------------|----------|
| WO 9622968 | A1 | 19960801 | WO 1996-US548 | 19960117 |
| W: BR, CA, CN, JP, KR, SG | | | | |
| RW: AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE | | | | |
| US 5821378 | A | 19981013 | US 1995-563718 | 19951128 |
| EP 804412 | A1 | 19971105 | EP 1996-902689 | 19960117 |
| EP 804412 | B1 | 19991201 | | |
| R: AT, BE, CH, DE, ES, FR, GB, IT, LI, NL, SE | | | | |
| BR 9606718 | A | 19980113 | BR 1996-6718 | 19960117 |
| JP 10512879 | T | 19981208 | JP 1996-522902 | 19960117 |
| JP 3959111 | B2 | 20070815 | | |
| PRIORITY APPLN. INFO.: | | | US 1995-379429 | 19950127 |
| | | | US 1995-563718 | 19951128 |
| | | | WO 1996-US548 | 19960117 |
| OTHER SOURCE(S): | MARPAT 125:195996 | | | |
| GI | | | | |



AB Improved liquid phase process useful in the hydrocyanation of diolefinsic compds. to produce nonconjugated acyclic nitriles and in the liquid phase isomerization of the nitriles to 3- and/or 4-monoalkene linear nitriles. The improvement involves conducting the process in the presence of zero-valent Ni and a multidentate phosphite ligand. As an example of hydrocyanation, 0.201 g 25 weight% 1,3-butadiene in butyronitrile, 0.080 g 25 weight% HCN in propionitrile and 0.077 g of catalyst solution (0.014 g Ni(COD)₂, 0.118 g I (R1 = OMe, R5 = tBu), 9.87 g propionitrile) were mixed and heated at 80°; after 1 h, 19.1% 3-pentenenitrile and 75.5% 2-methyl-3-butenenitrile were obtained; by comparison, use of Ni(P(OC₆H₄Me-p))₃)₄/P(OC₆H₄Me-p)₃ as catalyst gave 2.8 and 1.7%, resp. under similar conditions. As an example of isomerization, 93% of 2-methyl-3-butenenitrile isomerized to 3-pentenenitrile after 3 h in the presence of the Ni(COD)₂/I (R1 = OMe, R5 = tBu) catalyst, whereas 25% conversion occurred in the presence of Ni(P(OC₆H₄Me-p))₃)₄/P(OC₆H₄Me-p)₃. The invention also provides a novel method of making phosphorochloridites and diaryl N,N-dialkylphosphoramidites. As an example of synthesis of a diaryl N,N-dialkylphosphoramidite, to 25.0 g PCl₃ in 350 mL toluene was added 19.1 g dry iPr₂NH at 5-7°, after which 19.4 g Et₃N was added at 5-8°; after 16 h of stirring, a solution of 52.4 g thymol in 38.2 g Et₃N and 50 mL dry toluene was added <40°, followed by 0.25 g 4-dimethylaminopyridine in 40 mL toluene; after workup, iPr₂NP(OC₆H₃iPr-2-Me-5)₂ of 90-95% purity was obtained. As an example of synthesis of a phosphorochloridite, anhydrous HCl gas was bubbled into a solution of 7.21 g iPr₂NP(OC₆H₄iPr-2)₂ in 200 mL cyclohexane at 0° over 20 min to give ClP(OC₆H₄iPr-2).₂

RX(1) OF 6 2 A + 2 B ==> C + D...





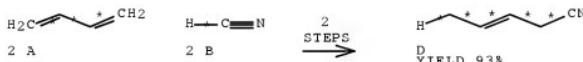
C YIELD 76%



D YIELD 22%

RX(1) RCT A 106-90-0, B 74-90-8
 PRO C 16529-56-9, D 4635-87-4
 CAT 1295-35-8 Ni dicyclooctadiene, 121627-17-6
 Dibenzo[d,f][1,3,2]dioxaphosphhepin, 6,6'-[3,3'-bis(1,1-dimethylethyl)-5,5'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis(oxy)]bis-
 SOL 109-74-0 Butanenitrile, 107-12-0 Propionitrile

RX(6) OF 6 COMPOSED OF RX(1), RX(5)
 RX(6) 2 A + 2 B =====> D



RX(1) RCT A 106-99-0, B 74-90-8
 PRO C 16529-56-9, D 4635-87-4
 CAT 1295-35-8 Ni dicyclooctadiene, 121627-17-6
 Dibenzo[d,f][1,3,2]dioxaphosphhepin, 6,6'-[3,3'-bis(1,1-dimethylethyl)-5,5'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis(oxy)]bis-
 SOL 109-74-0 Butanenitrile, 107-12-0 Propionitrile

RX(5) RCT C 16529-56-9
 PRO D 4635-87-4
 CAT 1295-35-8 Ni dicyclooctadiene, 121627-17-6
 Dibenzo[d,f][1,3,2]dioxaphosphhepin, 6,6'-[3,3'-bis(1,1-dimethylethyl)-5,5'-dimethoxy[1,1'-biphenyl]-2,2'-diyl]bis(oxy)]bis-
 SOL 107-12-0 Propionitrile

L88 ANSWER 38 OF 60 USPATFULL on STN

ACCESSION . . .

THIS PATENT.

AB A process is described for preparing 3-pentenenitrile by hydrocyanating 1,3-butadiene with hydrogen cyanide over at least one catalyst, wherein the 1,3-butadiene and/or hydrogen cyanide is contacted with at least one microporous solid before the reaction. CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB A process is described for preparing 3-pentenenitrile by hydrocyanating 1,3-butadiene with hydrogen cyanide over at least one catalyst, wherein the 1,3-

- butadiene and/or hydrogen cyanide is contacted with at least one microporous solid before the reaction.
- SUMM The present invention relates to a process for preparing 3-pentenenitrile by hydrocyanating 1,3-butadiene with hydrogen cyanide over at least one catalyst.
- SUMM . . . hydrocyanated to 3-pentenenitrile. In a second, subsequent hydrocyanation, 3-pentenenitrile is reacted with hydrogen cyanide to give adiponitrile. Both hydrocyanations are catalyzed by nickel(0)-phosphorus complexes.
- SUMM U.S. Pat. No. 3,852,329 describes a process for isomerizing 2-methyl-3-butenenitrile over a nickel(0)-phosphorus complex as a catalyst to give 3-pentenenitrile. In this isomerization, 2-methyl-3-butenenitrile and/or the catalyst is contacted with a molecular sieve before the actual isomerization. According to U.S. Pat. No. 3,852,329 it is also possible to carry out the isomerization directly in the presence of a molecular sieve.
- SUMM U.S. Pat. No. 3,846,474 describes a process for hydrocyanating 3-pentenenitrile over a nickel(0)-phosphorus catalyst. In this process, 3-pentenenitrile is contacted with a molecular sieve before the hydrocyanation. Alternatively, it is possible that the molecular sieve is used during the hydrocyanation or the catalyst solution is treated with a molecular sieve before it is used in the hydrocyanation.
- SUMM . . . the present invention to provide a process for preparing 3-pentenenitrile by hydrocyanating 1,3-butadiene with hydrogen cyanide over at least one catalyst, the catalyst used in the process having a high lifetime.
- SUMM . . . of this object starts from a process for preparing 3-pentenenitrile by hydrocyanating 1,3-butadiene with hydrogen cyanide over at least one catalyst. In a first embodiment, the process according to the invention comprises contacting 1,3-butadiene and/or hydrogen cyanide with at least one microporous solid before the reaction.
- SUMM It has been found in accordance with the invention that the contacting of 1,3-butadiene with the at least one microporous solid increases the lifetime of the nickel(0)-phosphorus catalyst. Without being bound to a theory, the effect of the increased lifetime of the catalyst is attributed to the removal of water and of the tert-butyldpyrocatechol stabilizer.
- SUMM . . . to the invention, the 1,3-butadiene and the hydrogen cyanide may be contacted together or separately with the at least one microporous solid. It is preferred that the 1,3-butadiene and/or the hydrogen cyanide are freed of the at least one microporous solid before the actual hydrocyanation with the at least one catalyst.
- SUMM . . . the present invention relates to a process for preparing 3-pentenenitrile by hydrocyanating 1,3-butadiene with hydrogen cyanide with at least one catalyst, the process according to the invention comprising effecting the hydrocyanation in the presence of the at least one microporous solid.
- SUMM When the hydrocyanation is carried out in semibatchwise operation, it is preferred that the reactor is initially charged with the catalyst components and 1,3-butadiene, while hydrogen cyanide is metered into the reaction mixture over the reaction time.
- SUMM . . . a solvent is used, the solvent should be liquid and inert toward the unsaturated compounds and the at least one catalyst at the given reaction temperature and the given reaction pressure. In general, the solvents used are hydrocarbons, for example benzene. . . .
- SUMM . . . charging the apparatus with all reactants. However, it is preferred when the apparatus is filled with the at least one catalyst, 1,3-butadiene and, if appropriate, the solvent. The gaseous hydrogen cyanide preferably floats over the surface of the reaction mixture or.

- . . . reaction mixture. A further procedure for charging the apparatus is the filling of the apparatus with the at least one catalyst, hydrogen cyanide and, if appropriate, the solvent, and slowly feeding the 1,3-butadiene to the reaction mixture. Alternatively, it is also. . .
- SUMM . . . the pressure in the reactor is such that all reactants such as 1,3-butadiene, hydrogen cyanide and the at least one catalyst are metered in in liquid form and are present in the liquid phase in the reaction mixture. A solid suspended. . . phase may be present in the reaction mixture and may also be metered in together with the at least one catalyst, for example consisting of degradation products of the catalyst system, comprising nickel(II) compounds inter alia.
- SUMM The microporous solid obtained after the treatment of the 1,3-butadiene and/or hydrogen cyanide, or the microporous solid used in the hydrocyanation, may, after it has been used, be regenerated by heating under reduced pressure in an atmosphere which is formed by gases selected from the group consisting of noble gases, air and oxygen. It is thus possible to use the microporous solid again.
- SUMM The at least one microporous solid used in the process according to the invention is preferably selected from the group consisting of aluminas and molecular sieves, and preferably has a particle size of from 0.01 to 20 mm, more preferably from 0.1 to 10 mm, in. . .
- SUMM When alumina is used as the microporous solid in the process according to the invention, the alumina may be contaminated with rare earth metal compounds, alkali metal. . .
- SUMM When the microporous solid used in the process according to the invention is a molecular sieve, this refers to molecular sieve having an average pore radius of from 0.1 to 20 Å, preferably from 1 to 10 Å.
- SUMM When the 1,3-butadiene, before the actual hydrocyanation over the at least one nickel(0)-phosphorus catalyst, is contacted with the at least one microporous solid, it is advantageous subsequently to store and transport it, before the actual hydrocyanation of the 1,3-butadiene, at temperatures of. . .
- SUMM The inventive treatment of the feed streams for the above-described hydrocyanation with molecular sieve or alumina result in residual water contents in the reaction mixture of less than 1000 ppm, more preferably less than. . .
- DETD This example illustrates the need to dry butadiene before it is contacted with a catalyst system, suitable for the hydrocyanation, of Ni(0) complex with, for example, trityl phosphite as a ligand.
- DETD . . . from brine cooling to heating with throttle-controlled 35 bar steam. The bed was then flowed through with 1 m.sup.3/h of nitrogen and heated gradually to 210°C. over three days. When the end temperature had been attained, the steam heating was switched off and the bed was flowed through with nitrogen until 60°C. had been attained in the interior of the bed. Reconnecting the jacket again to brine cooling cooled. . .
- DETD On the Drying with Molecular Sieve
- DETD A vessel made of boilerplate (diameter 50 mm) was charged with a 200 mm-high bed of molecular sieve from Karl Roth GmbH (product number 4062020) and cooled to 0°C. using a jacket. Subsequently, butadiene was introduced at. . .
- DETD 2.24 mol of butadiene dried over a bed of 4 Å molecular sieve, 1.62 mol of HCN and 14 mmol of Ni in the form of nickel(0)(m-p-tolyl phosphite) were fed per hour into. . .
- CLM What is claimed is:
1. A process for preparing 3-pentenenitrile by hydrocyanating 1,3-butadiene with hydrogen cyanide over at least one catalyst, the

process comprising contacting 1,3-butadiene with at least one microporous solid, and releasing the 1,3-butadiene from the at least one microporous solid before the hydrocyanation; and regenerating the at least one microporous solid which had been contacted with 1,3-butadiene or hydrogen cyanide by heating under reduced pressure in an atmosphere comprising one or more gases selected from the group consisting of noble gases, air and nitrogen.

. . . to claim 1, further comprising contacting hydrogen cyanide together with or separately from the 1,3-butadiene with the at least one microporous solid.

3. The process according to claim 1, wherein the at least one microporous solid includes tubes having beds, and the flow conditions of 1,3-butadiene are selected in such a way to provide plug flow characteristics over the at least one microporous solid.

4. A process for preparing 3-pentenenitrile by hydrocyanating 1,3-butadiene with hydrogen cyanide over at least one catalyst, in the presence of at least one microporous solid.

5. The process according to claim 4, further comprising regenerating the at least one microporous solid by heating under reduced pressure in an atmosphere comprising one or more gases from the group consisting of noble gases, air and nitrogen.

7. The process according to claim 1, wherein the at least one microporous solid is selected from the group consisting of aluminas and molecular sieves and has a pore size of from 0.01 to 20 mm.

8. The process according to claim 1, wherein the microporous solid has a porosity which is between 0 and 80% based on the particle volume.

9. The process according to claim 1, wherein the microporous solid is in extrudate form, in round form or in undefined form as a result of fracturing.

10. The process according to claim 2, wherein the at least one microporous solid includes tubes having beds, and the flow conditions of the hydrogen cyanide are selected in such a way to. . .

12. The process according to claim 4, wherein the at least one microporous solid is selected from the group consisting of aluminas and molecular sieves and has a pore size of from 0.01 to 20 mm.

13. A process for preparing 3-pentenenitrile by hydrocyanating 1,3-butadiene with hydrogen cyanide over at least one catalyst, the process comprising: contacting at least one microporous solid with the 1,3-butadiene and hydrogen cyanide; directing the the 1,3-butadiene and the hydrogen cyanide that had contacted the at least one microporous solid to a hydrocyanation reaction system; and regenerating the at least one microporous solid that had been contacted with the 1,3-butadiene and hydrogen cyanide by heating under reduced pressure in an atmosphere comprising one or more gases selected from the group consisting of noble gases, air and nitrogen.

14. The process according to claim 13, wherein the at least one microporous solid includes tubes having beds, and the flow conditions of 1,3-butadiene and hydrogen cyanide are selected to provide plug flow characteristics over the at least one microporous solid.

16. The process according to claim 13 wherein the at least one microporous solid is selected from the group consisting of aluminas and molecular sieves and has a pore size of from 0.01 to 20 mm.

17. The process according to claim 16 wherein the microporous solid has a porosity which is between 0 and 80% based on the particle volume.

IT Air
 (catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenenitrile using)

IT 4635-87-4P, 3-Pentenenitrile
 (catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenenitrile)

IT 74-96-8, Hydrogen cyanide, reactions 106-99-0,
 1,3-Butadiene, reactions
 (catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenenitrile)

PI US 2007155977 A1 20070705 <--|

AB A process is described for preparing 3-pentenenitrile by hydrocyanating 1,3-butadiene with hydrogen cyanide over at least one catalyst, wherein the 1,3-butadiene and/or hydrogen cyanide is contacted with at least one microporous solid before the reaction.|

SUMM The present invention relates to a process for preparing 3-pentenenitrile by hydrocyanating 1,3-butadiene with hydrogen cyanide over at least one catalyst.

SUMM Adiponitrile is an important starting material in nylon production and is obtained by double hydrocyanation of 1,3-butadiene. In a first hydrocyanation, 1,3-butadiene is hydrocyanated to 3-pentenenitrile. In a second, subsequent hydrocyanation, 3-pentenenitrile is reacted with hydrogen cyanide to give adiponitrile. Both hydrocyanations are catalyzed by nickel(0)-phosphorus complexes.

SUMM U.S. Pat. No. 3,852,329 describes a process for isomerizing 2-methyl-3-butenenitrile over a nickel(0)-phosphorus complex as a catalyst to give 3-pentenenitrile. In this isomerization, 2-methyl-3-butenenitrile and/or the catalyst is contacted with a molecular sieve before the actual isomerization. According to U.S. Pat. No. 3,852,329 it is also possible to carry out the isomerization directly in the presence of a molecular sieve.

SUMM U.S. Pat. No. 3,846,474 describes a process for hydrocyanating 3-pentenenitrile over a nickel(0)-phosphorus catalyst. In this process, 3-pentenenitrile is contacted with a molecular sieve before the hydrocyanation. Alternatively, it is possible that the molecular sieve is used during the hydrocyanation or the catalyst solution is treated with a molecular sieve before it is used in the hydrocyanation.

SUMM It is thus an object of the present invention to provide a process for preparing 3-pentenenitrile by hydrocyanating 1,3-butadiene with hydrogen cyanide over at least one catalyst, the catalyst used in the process having a high lifetime.

SUMM The inventive achievement of this object starts from a process for preparing 3-pentenenitrile by hydrocyanating 1,3-butadiene with hydrogen cyanide over at least one catalyst. In a first embodiment, the process according to the invention comprises contacting 1,3-butadiene and/or

hydrogen cyanide with at least one microporous solid before the reaction.

SUMM It has been found in accordance with the invention that the contacting of 1,3-butadiene with the at least one microporous solid increases the lifetime of the nickel(0)-phosphorus catalyst. Without being bound to a theory, the effect of the increased lifetime of the catalyst is attributed to the removal of water and of the tert-butylpyrocatechol stabilizer.

SUMM In the process according to the invention, the 1,3-butadiene and the hydrogen cyanide may be contacted together or separately with the at least one microporous solid. It is preferred that the 1,3-butadiene and/or the hydrogen cyanide are freed of the at least one microporous solid before the actual hydrocyanation with the at least one catalyst.

SUMM In a second embodiment, the present invention relates to a process for preparing 3-pentenonitrile by hydrocyanating 1,3-butadiene with hydrogen cyanide with at least one catalyst, the process according to the invention comprising effecting the hydrocyanation in the presence of the at least one microporous solid.

SUMM When the hydrocyanation is carried out in semibatchwise operation, it is preferred that the reactor is initially charged with the catalyst components and 1,3-butadiene, while hydrogen cyanide is metered into the reaction mixture over the reaction time.

SUMM The hydrocyanation may be carried out in the presence or in the absence of a solvent. When a solvent is used, the solvent should be liquid and inert toward the unsaturated compounds and the at least one catalyst at the given reaction temperature and the given reaction pressure. In general, the solvents used are hydrocarbons, for example benzene or xylene, or nitrites, for example acetonitrile or benzonitrile. However, preference is given to using a ligand as the solvent.

SUMM The hydrocyanation reaction may be carried out by charging the apparatus with all reactants. However, it is preferred when the apparatus is filled with the at least one catalyst, 1,3-butadiene and, if appropriate, the solvent. The gaseous hydrogen cyanide preferably floats over the surface of the reaction mixture or is preferably passed through the reaction mixture. A further procedure for charging the apparatus is the filling of the apparatus with the at least one catalyst, hydrogen cyanide and, if appropriate, the solvent, and slowly feeding the 1,3-butadiene to the reaction mixture. Alternatively, it is also possible that the reactants are introduced into the reactor and the reaction mixture is brought to the reaction temperature at which the hydrogen cyanide is added to the mixture in liquid form. In addition, the hydrogen cyanide may also be added before heating to reaction temperature. The reaction is carried out under conventional hydrocyanation conditions for temperature, atmosphere, reaction time, etc.

SUMM In a further embodiment, the hydrocyanation may be carried out in the liquid phase, in which case the pressure in the reactor is such that all reactants such as 1,3-butadiene, hydrogen cyanide and the at least one catalyst are metered in liquid form and are present in the liquid phase in the reaction mixture. A solid suspended phase may be present in the reaction mixture and may also be metered in together with the at least one catalyst, for example consisting of degradation products of the catalyst system, comprising nickel(II) compounds inter alia.

- SUMM The microporous solid obtained after the treatment of the 1,3-butadiene and/or hydrogen cyanide, or the microporous solid used in the hydrocyanation, may, after it has been used, be regenerated by heating under reduced pressure in an atmosphere which is formed by gases selected from the group consisting of noble gases, air and oxygen. It is thus possible to use the microporous solid again.
- SUMM The at least one microporous solid used in the process according to the invention is preferably selected from the group consisting of aluminas and molecular sieves, and preferably has a particle size of from 0.01 to 20 mm, more preferably from 0.1 to 10 mm, in particular from 1 to 5 mm. The porosity of the shaped bodies is between 0 and 80% based on the particle volume. It is possible to use particles either in the form of extrudates or in round form, or in undefined form as a result of fracturing.
- SUMM When alumina is used as the microporous solid in the process according to the invention, the alumina may be contaminated with rare earth metal compounds, alkali metal compounds or alkaline earth metal compounds in the range from 0 to 20% by weight, more preferably from 0 to 10% by weight, based in each case on the solid mass used.
- SUMM When the microporous solid used in the process according to the invention is a molecular sieve, this refers to molecular sieve having an average pore radius of from 0.1 to 20 Å, preferably from 1 to 10 Å.
- SUMM When the 1,3-butadiene, before the actual hydrocyanation over the at least one nickel(0)-phosphorus catalyst, is contacted with the at least one microporous solid, it is advantageous subsequently to store and transport it, before the actual hydrocyanation of the 1,3-butadiene, at temperatures of less than 50° C., more preferably less than 20° C., in particular less than 0° C., in order to prevent polymerizations.
- SUMM The inventive treatment of the feed streams for the above-described hydrocyanation with molecular sieve or alumina result in residual water contents in the reaction mixture of less than 1000 ppm, more preferably less than 100 ppm, in particular less than 10 ppm, of water.
- DETD This example illustrates the need to dry butadiene before it is contacted with a catalyst system, suitable for the hydrocyanation, of Ni(0) complex with, for example, trityl phosphite as a ligand.
- DETD The apparatus described in Example 1 with the bed detailed there was charged with butadiene until the water content in the outlet stream had risen to a measured value of 50 ppm by weight of water. The butadiene feed was then stopped. Subsequently, the jacket was switched from brine cooling to heating with throttle-controlled 35 bar steam. The bed was then flowed through with 1 m.sup.3/h of nitrogen and heated gradually to 210° C. over three days. When the end temperature had been attained, the steam heating was switched off and the bed was flowed through with nitrogen until 60° C. had been attained in the interior of the bed. Reconnecting the jacket again to brine cooling cooled the bed back to 0° C. and butadiene was then introduced again. After the wetting had been completed, the water meter at the outlet was brought back into operation. The measurements were again at 1 ppm by weight of water based on butadiene.
- DETD On the Drying with Molecular Sieve

DETD A vessel made of boilerplate (diameter 50 mm) was charged with a 200 mm-high bed of molecular sieve from Karl Roth GmbH (product number 4062020) and cooled to 0°C. using a jacket. Subsequently, butadiene was introduced at a mass flow rate of 100 g/h. At the outlet of the bed, a measuring instrument for determining water in butadiene (from General Eastern, AMY 170) did not find any detectable amounts of water over a period of two weeks. Accordingly, the butadiene was dry after it had flowed through the bed.

DETD 2.24 mol of butadiene dried over a bed of 4 Å molecular sieve, 1.62 mol of HCN and 14 mmol of Ni in the form of nickel(0) (m-/p-tolyl phosphite) were fed per hour into a stirred pressure reactor (pressure: 15 bar, internal temperature 105°C., residence time: approx. 40 min/reactor). According to quantitative analysis, the HCN conversion is quantitative (Vollhard titration). The 2M3BN/3PN ratio of the reaction effluent is determined by GC chromatography (GC area percent). The 2M3BN/3PN ratio was 1.82/1. The loss of Ni(0) based on product of value formed was 0.33 kg of Ni(0)/t of product of value (3PN/2M3BN).

1. A process for preparing 3-pentenenitrile by hydrocyanating 1,3-butadiene with hydrogen cyanide over at least one catalyst, the process comprising contacting 1,3-butadiene with at least one microporous solid, and releasing the 1,3-butadiene from the at least one microporous solid before the hydrocyanation; and regenerating the at least one microporous solid which had been contacted with 1,3-butadiene or hydrogen cyanide by heating under reduced pressure in an atmosphere comprising one or more gases selected from the group consisting of noble gases, air and nitrogen.

2. The process according to claim 1, further comprising contacting hydrogen cyanide together with or separately from the 1,3-butadiene with the at least one microporous solid.

3. The process according to claim 1, wherein the at least one microporous solid includes tubes having beds, and the flow conditions of 1,3-butadiene are selected in such a way to provide plug flow characteristics over the at least one microporous solid.

4. A process for preparing 3-pentenenitrile by hydrocyanating 1,3-butadiene with hydrogen cyanide over at least one catalyst, in the presence of at least one microporous solid.

5. The process according to claim 4, further comprising regenerating the at least one microporous solid by heating under reduced pressure in an atmosphere comprising one or more gases from the group consisting of noble gases, air and nitrogen.

7. The process according to claim 1, wherein the at least one microporous solid is selected from the group consisting of aluminas and molecular sieves and has a pore size of from 0.01 to 20 mm.

8. The process according to claim 1, wherein the microporous solid has a porosity which is between 0 and 80% based on the particle volume.

9. The process according to claim 1, wherein the microporous solid is in extrudate form, in round form or in undefined form as a result of fracturing.

10. The process according to claim 2, wherein the at least one microporous solid includes tubes having beds, and the flow conditions of the hydrogen cyanide are selected in such a way to provide flow characteristics.

12. The process according to claim 4, wherein the at least one microporous solid is selected from the group consisting of aluminas and molecular sieves and has a pore size of from 0.01 to 20 mm.

13. A process for preparing 3-pentenenitrile by hydrocyanating 1,3-butadiene with hydrogen cyanide over at least one catalyst, the process comprising: contacting at least one microporous solid with the 1,3-butadiene and hydrogen cyanide; directing the the 1,3-butadiene and the hydrogen cyanide that had contacted the at least one microporous solid to a hydrocyanation reaction system; and regenerating the at least one microporous solid that had been contacted with the 1,3-butadiene and hydrogen cyanide by heating under reduced pressure in an atmosphere comprising one or more gases selected from the group consisting of noble gases, air and nitrogen.

14. The process according to claim 13, wherein the at least one microporous solid includes tubes having beds, and the flow conditions of 1,3-butadiene and hydrogen cyanide are selected to provide plug flow characteristics over the at least one microporous solid.

16. The process according to claim 13 wherein the at least one microporous solid is selected from the group consisting of aluminas and molecular sieves and has a pore size of from 0.01 to 20 mm.

17. The process according to claim 16 wherein the microporous solid has a porosity which is between 0 and 80% based on the particle volume.

- IT Air
 (catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenenitrile using)
- IT 4635-87-4P, 3-Pentenenitrile
 (catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenenitrile)
- IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,
 1,3-Butadiene, reactions
 (catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenenitrile)
- IT 4635-87-4P, 3-Pentenenitrile
 (catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenenitrile)
- RN 4635-87-4 USPATFULL
- CN 3-Pentenenitrile (CA INDEX NAME)



- IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,
 1,3-Butadiene, reactions
 (catalytic hydrocyanation of 1,3-butadiene with hydrogen cyanide in the presence of at least one microporous solid for the manufacture of 3-pentenenitrile)
- RN 74-90-8 USPATFULL

CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 USPATFULL
 CN 1,3-Butadiene (CA INDEX NAME)



L88 ANSWER 39 OF 60 USPATFULL on STN
 ACCESSION NUMBER: 2007128858 USPATFULL Full-text
 TITLE: Method for the separation of pentenenitrile isomers
 INVENTOR(S): Jungkamp, Tim, Kapellen, BELGIUM
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| | NUMBER | KIND | DATE | |
|---------------------|----------------|------|----------|--------------|
| PATENT INFORMATION: | US 2007112215 | A1 | 20070517 | <-- |
| APPLICATION INFO.: | US 2005-586452 | A1 | 20050126 | (10) |
| | WO 2005-EP726 | | 20050126 | |
| | | | 20060718 | PCT 371 date |

| | NUMBER | DATE |
|-----------------------|--|------|
| PRIORITY INFORMATION: | DE 2004-10200400472120040129 | |
| DOCUMENT TYPE: | Utility | |
| FILE SEGMENT: | APPLICATION | |
| LEGAL REPRESENTATIVE: | CONNOLLY BOVE LODGE & HUTZ LLP, P.O. BOX 2207, WILMINGTON, DE, 19899-2207, US | |
| NUMBER OF CLAIMS: | 14 | |
| EXEMPLARY CLAIM: | 1 | |
| LINE COUNT: | 1081 | |

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB A process is described for separating mixtures of isomeric pentenenitriles, in which at least one isomer is removed from the mixture, wherein the separation of the substance mixtures of isomeric pentenenitriles is effected distillatively under reduced pressure.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

- SUMM . . . and 4-vinylcyclohexene. In a second hydrocyanation, 3-pentenenitrile is subsequently reacted with hydrogen cyanide to give adiponitrile, likewise over a nickel catalyst, but with addition of a Lewis acid. In this second hydrocyanation too, a mixture of the reactant and product nitriles. . .
- SUMM . . . Pat. No. 3,852,325 and U.S. Pat. No. 3,852,327 to convert the pentenenitrile isomers which are difficult to remove by distillation catalytically to those which can easily be removed by distillation.
- SUMM A disadvantage is that the catalytic isomerization leads to losses of products of value as a result of formation of undesired isomers or oligomers.
- SUMM . . . the resulting organic phase first has to be freed completely of water before further use in hydrocyanation reactions using nickel(0) catalysts with phosphorus(III) ligands, since the phosphorus(III) ligands are otherwise irreversibly hydrolyzed and thus deactivated. A further disadvantage in this process. . .
- SUMM The hydrocyanation of butadiene to 3-pentenenitrile and mixtures thereof with 2-methyl-3-butenenitrile are carried out in the presence of a nickel(0) catalyst.
- SUMM The Ni(0) catalysts are complexes, which contain phosphorus ligands and/or free phosphorus ligands preferably homogeneously dissolved nickel(0) complexes.
- SUMM . . . to in the context of the present invention as 3-pentenenitrile. However, the 2-methyl-3-butenenitrile occurring in the hydrocyanation, depending on the catalyst system, in at least double-digit percentages, based on the sum of all pentenenitrile isomers formed, has to be removed before. . .
- SUMM . . . comprise 2-methyl-3-butenenitrile and 3-pentenenitrile. These mixtures are preferably obtained in a reaction of 1,3-butadiene with hydrogen cyanide over a hydrocyanation catalyst, the hydrocyanation effluent typically comprising a proportion of 1,3-butadiene unconverted in the hydrocyanation which can be removed at least partly by suitable processes, and the catalyst content present in the product stream obtained in this way being removable by suitable processes. Processes of this type are. . . 004 720 and DE-A-102 004 004 724. However, it is not necessarily obligatory to remove the unconverted 1,3-butadiene and the catalyst content.
- SUMM The nickel(0)-containing catalyst systems can be prepared by processes known per se.
- SUMM The ligands used for the isomerization catalyst may be the same phosphorus ligands as for the above-described hydrocyanation.
- SUMM . . . 4,874,884, it is possible to use synergistically active combinations of Lewis acids, in order to increase the activity of the catalyst system. Suitable promoters may, for example, be selected from the group consisting of CdCl₂.sub.2, FeCl₃.sub.2, ZnCl₂.sub.2, B(C₆H₅).sub.3 and (C₆H₅).sub.2SnX where. . .
- SUMM . . . advantageous when the isomerization is carried out in a nonoxidative atmosphere, for example under a protective gas atmosphere composed of nitrogen or a noble gas such as argon.
- SUMM The cis-2-pentenenitrile removed may be isomerized thermally or under catalysis to the 3-pentenenitrile product of value. Mixtures having substantially trans-2-pentenenitrile, trans-3-pentenenitrile and unconverted cis-2-pentenenitrile are obtained. A prerequisite for the. . .
- SUMM . . . comprises cis-2-pentenenitrile and 3-pentenenitrile. These mixtures stem, for example, from a reaction of 3-pentenenitrile with hydrogen cyanide over a hydrocyanation catalyst. In addition, these mixtures may stem from the thermal or catalyzed isomerization of cis-2-pentenenitrile.
- SUMM . . . hydrocyanation reaction. Secondly, it is also possible to add

to this circulation stream pentenenitriles which remain after the removal of catalyst constituents in the adiponitrile-containing product stream and are removed from this stream for the purpose of recycling, as described in . . .

SUMM . . . invention is accordingly intended preferentially for mixtures which stem from a reaction of 1,3-butadiene with hydrogen cyanide over a hydrocyanation catalyst, or from an isomerization of 2-methyl-3-butenenitrile or from a reaction of 3-pentenenitrile with hydrogen cyanide over a hydrocyanation catalyst.

CLM What is claimed is:

- · . the mixture comprises 2-methyl-3-butenenitrile and 3-pentenenitrile and is produced from a reaction of 1,3-butadiene with hydrogen cyanide over a hydrocyanation catalyst.
- · . mixture comprises cis-2-pentenenitrile and 3-pentenenitrile and stems is produced from a reaction of 3-pentenenitrile with hydrogen cyanide over a hydrocyanation catalyst.
- · . the mixture comprises (E)-2-methyl-2-butenenitrile and 3-pentenenitrile and is produced from a reaction of 1,3-butadiene with hydrogen cyanide over a hydrocyanation catalyst or from the isomerization of 2-methyl-3-butenenitrile or from a reaction of 3-pentenenitrile with hydrogen cyanide over a hydrocyanation catalyst.
- · . the mixture comprises 2-methyl-3-butenenitrile and 3-pentenenitrile and is produced from a reaction of 1,3-butadiene with hydrogen cyanide over a hydrocyanation catalyst.
- · . the mixture comprises cis-2-pentenenitrile and 3-pentenenitrile and is produced from a reaction of 3-pentenenitrile with hydrogen cyanide over a hydrocyanation catalyst.
- · . mixture comprises (E)-2-methyl-2-butenenitrile and 3-pentenenitrile and is produced from a reaction of 1, 3-butadiene with hydrogen cyanide over a hydrocyanation catalyst or from the isomerization of 2-methyl-3-butenenitrile or from a reaction of 3-pentenenitrile with hydrogen cyanide over a hydrocyanation catalyst.

IT 4635-97-4P, 3-Pentenenitrile 16529-56-9P, 2-Methyl-3-butenenitrile 16529-66-1P, trans-3-Pentenenitrile 16545-78-1P, cis-3-Pentenenitrile 20068-02-4P, cis-2-Methyl-2-butenenitrile 25899-50-7P, cis-2-Pentenenitrile 27236-41-5P, Pentenenitrile 30574-97-1P, trans-2-Methyl-2-butenenitrile (vacuum distillation method for the separation of pentenenitrile isomers)

IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,
1,3-Butadiene, reactions
(vacuum distillation method for the separation of pentenenitrile isomers prepared

from)

PI US 2007112215 A1 20070517 <--!
SUMM Adiponitrile, an important intermediate in nylon production, is prepared by double hydrocyanation of 1,3-butadiene. In a first hydrocyanation stage, 1,3-butadiene is reacted with hydrogen cyanide in the presence of nickel(0) which is stabilized with phosphorus ligands to give 3-pentenenitrile. Secondary components of this first hydrocyanation are substantially 2-methyl-3-butenenitrile, 2-pentenenitriles, 2-methyl-2-butenenitriles, C_{sub.9} nitrites, methylglutaronitrile and 4-vinylcyclohexene. In a second hydrocyanation, 3-pentenenitrile is subsequently reacted with hydrogen cyanide to give adiponitrile, likewise over a nickel catalyst, but with addition of a Lewis acid. In

this second hydrocyanation too, a mixture of the reactant and product nitriles and also the abovementioned secondary components is obtained.

- SUMM To circumvent a separation of trans-3-pentenenitrile and trans-2-pentenenitrile, it is proposed, for example in U.S. Pat. No. 3,526,654, U.S. Pat. No. 3,564,040, U.S. Pat. No. 3,852,325 and U.S. Pat. No. 3,852,327 to convert the pentenenitrile isomers which are difficult to remove by distillation catalytically to those which can easily be removed by distillation.
- SUMM A disadvantage is that the catalytic isomerization leads to losses of products of value as a result of formation of undesired isomers or oligomers.
- SUMM To circumvent a separation of (Z)-2-methyl-2-butenenitrile and 2-methyl-3-butenenitrile, and also trans-2-pentenenitrile and trans-3-pentenenitrile, U.S. Pat. No. 3,865,865 proposes treating the nitrile mixture with aqueous sulfite solution, in each case to obtain an aqueous phase comprising the particular bisulfite adducts of the conjugated nitriles (Z)-2-methyl-2-butenenitrile or trans-2-pentenenitrile, and an organic phase depleted in these nitriles. A disadvantage in this process is that the resulting organic phase first has to be freed completely of water before further use in hydrocyanation reactions using nickel(0) catalysts with phosphorus(III) ligands, since the phosphorus(III) ligands are otherwise irreversibly hydrolyzed and thus deactivated. A further disadvantage in this process is that the resulting bisulfite adducts can only be dissociated for the purpose of further using the conjugated nitriles, as described in U.S. Pat. No. 3,865,865, only under drastic conditions and only with moderate yield.
- SUMM The hydrocyanation of butadiene to 3-pentenenitrile and mixtures thereof with 2-methyl-3-butenenitrile are carried out in the presence of a nickel(0) catalyst.
- SUMM The Ni(0) catalysts are complexes, which contain phosphorus ligands and/or free phosphorus ligands preferably homogeneously dissolved nickel(0) complexes.
- SUMM The desired products of this hydrocyanation which can be used for preparing adiponitrile are trans-3-pentenenitrile, cis-3-pentenenitrile and 4-pentenenitrile, which are referred to in the context of the present invention as 3-pentenenitrile. However, the 2-methyl-3-butenenitrile occurring in the hydrocyanation, depending on the catalyst system, in at least double-digit percentages, based on the sum of all pentenenitrile isomers formed, has to be removed before the further processing of the hydrocyanation effluent. The specification for the depletion of 2-methyl-3-butenenitrile in the 3-pentenenitrile is strict and has to be complied with because methylglutaronitrile (MGN), an undesired by-product of adiponitrile production, would form from 2-methyl-3-butenenitrile in the subsequent hydrocyanation. However, the complex apparatus and the energy requirements for the virtually complete removal of 2-methyl-3-butenenitrile from 3-pentenenitrile is very high and is determined by the relative volatility, defined as the ratio of the vapor pressures of these two substances, which is approx. 1.7 at atmospheric pressure, derived from the known standard boiling points of 416.8 K for trans-3-pentenenitrile and 396.1 K for 2-methyl-3-butenenitrile. It has been found in accordance with the invention that the relative volatility of 2-methyl-3-butenenitrile and 3-pentenenitrile increases at pressures below atmospheric pressure.

SUMM Accordingly, the process according to the invention is determined in one embodiment I for separating mixtures which comprise 2-methyl-3-butenenitrile and 3-pentenenitrile. These mixtures are preferably obtained in a reaction of 1,3-butadiene with hydrogen cyanide over a hydrocyanation catalyst, the hydrocyanation effluent typically comprising a proportion of 1,3-butadiene unconverted in the hydrocyanation which can be removed at least partly by suitable processes, and the catalyst content present in the product stream obtained in this way being removable by suitable processes. Processes of this type are described, for example, in DE-A-102 004 004 720 and DE-A-102 004 004 724. However, it is not necessarily obligatory to remove the unconverted 1,3-butadiene and the catalyst content.

SUMM The nickel(0)-containing catalyst systems can be prepared by processes known per se.

SUMM The ligands used for the isomerization catalyst may be the same phosphorus ligands as for the above-described hydrocyanation.

SUMM Useful Lewis acids are inorganic or organic metal compounds in which the cation is selected from the group consisting of scandium, titanium, vanadium, chromium, manganese, iron, cobalt, copper, zinc, boron, aluminum, yttrium, zirconium, niobium, molybdenum, cadmium, rhenium and tin. Examples include ZnBr₂.sub.2, ZnL₂.sub.2, ZnSO₄.sub.4, CuCl₂.sub.2, CuCl, Cu(O₂sub.3SCF₂.sub.3).sub.2, CoCl₂.sub.2, Col₂.sub.2, FeI₂.sub.2, FeCl₂.sub.3, FeCl₂.sub.2, FeCl₂.sub.2(THF).sub.2, TiCl₄.sub.4(THF).sub.2, TiCl₄.sub.2, TiCl₃.sub.3, ClTi(O-i-propyl).sub.3, MnCl₂.sub.2, ScCl₂.sub.3, AlCl₃.sub.3, (C₂H₅OH).sub.17)AlCl₂.sub.2, (C₂H₅OH).sub.17).sub.2AlCl₃, (i-C₃H₇OH).sub.9).sub.2AlCl₃, (C₂H₅OH).sub.5).sub.2AlCl₃, (C₂H₅OH).sub.5)AlCl₂.sub.2, ReCl₅.sub.5, ZrCl₄.sub.2, NbCl₅.sub.2, VCl₃.sub.3, CrCl₃.sub.2, MoCl₅.sub.5, YCl₃.sub.3, CdCl₂.sub.2, LaCl₃.sub.3, Er(O₂sub.3SCF₂.sub.3).sub.3, Yb(O₂sub.2CCF₃.sub.3).sub.3, SmCl₃.sub.3, B(C₂H₅OH).sub.5).sub.3, TaCl₅.sub.5, as described, for example, in U.S. Pat. No. 6,127,567, U.S. Pat. No. 6,171,996 and U.S. Pat. No. 6,380,421. Also useful are metal salts such as ZnCl₂.sub.2, Col₂.sub.2 and SnCl₂.sub.2, and organometallic compounds such as RAlCl₂.sub.2, R₂sub.2AlCl₃, RSnO₂.sub.3SCF₂.sub.3 and R₂sub.3B, where R is an alkyl or aryl group, as described, for example, in U.S. Pat. No. 3,496,217, U.S. Pat. No. 3,496,218 and U.S. Pat. No. 4,774,353. According to U.S. Pat. No. 3,773,809, the promoter used may also be a metal in cationic form which is selected from the group consisting of zinc, cadmium, beryllium, aluminum, gallium, indium, thallium, titanium, zirconium, hafnium, erbium, germanium, tin, vanadium, niobium, scandium, chromium, molybdenum, tungsten, manganese, rhodium, palladium, thorium, iron and cobalt, preferably zinc, cadmium, titanium, tin, chromium, iron and cobalt, and the anionic moiety of the compound may be selected from the group consisting of halides such as fluoride, chloride, bromide and iodide, anions of lower fatty acids having from 2 to 7 carbon atoms, HPO₄.sub.2⁻, H₂PO₄.sub.2⁻, CF₃COO⁻, C₂H₅OH⁻, 150SO₄.sub.2⁻ or SO₄.sub.4⁻. Further suitable promoters disclosed by U.S. Pat. No. 3,773,809 are borohydrides, organoborohydrides and boric esters of the formula R₂sub.3B and B(OR)₃, where R is selected from the group consisting of hydrogen, aryl radicals having from 6 to 18 carbon atoms, aryl radicals substituted by alkyl groups having from 1 to 7 carbon atoms and aryl radicals substituted by cyano-substituted alkyl groups having from 1 to 7 carbon atoms, advantageously triphenylboron. Moreover, as described in U.S. Pat. No. 4,874,884, it is possible to use synergistically active combinations of Lewis acids, in order to increase the activity of the catalyst system. Suitable promoters may, for

example, be selected from the group consisting of CdCl₂.sub.2, FeCl₂.sub.2, ZnCl₂.sub.2, B(C₂H₅.sub.5).sub.3 and (C₂H₅.sub.5).sub.3SnX where X.dbd.CF₃.sub.3SO₂.sub.3, CH₂.sub.3C₂H₅.sub.4SO₂.sub.3 or (C₂H₅.sub.5).sub.3BCN, and the preferred ratio specified of promoter to nickel is from about 1:16 to about 50:1.

SUMM In addition, it has been found to be advantageous when the isomerization is carried out in a nonoxidative atmosphere, for example under a protective gas atmosphere composed of nitrogen or a noble gas such as argon.

SUMM The cis-2-pentenenitrile removed may be isomerized thermally or under catalysis to the 3-pentenenitrile product of value. Mixtures having substantially trans-2-pentenenitrile, trans-3-pentenenitrile and unconverted cis-2-pentenenitrile are obtained. A prerequisite for the insertion of this isomerization step into an integrated process for preparing adiponitrile is that the removal of cis-2-pentenenitrile from this mixture is realizable economically.

SUMM According to embodiment II, the present invention thus relates to a process for separating mixtures of isomeric pentenenitriles, wherein the separation is effected distillatively under reduced pressure and the mixture comprises cis-2-pentenenitrile and 3-pentenenitrile. These mixtures stem, for example, from a reaction of 3-pentenenitrile with hydrogen cyanide over a hydrocyanation catalyst. In addition, these mixtures may stem from the thermal or catalyzed isomerization of cis-2-pentenenitrile.

SUMM In the hydrocyanation process of 3-pentenenitrile to adiponitrile, (E)-2-methyl-2-butenenitrile accordingly accumulates in some cases in the 3-pentenenitrile circulation stream. This circulation stream, as a mixture of pentenenitriles, may be composed, for example, firstly of the proportion of pentenenitriles which are removed directly after the hydrocyanation reaction. Secondly, it is also possible to add to this circulation stream pentenenitriles which remain after the removal of catalyst constituents in the adiponitrile-containing product stream and are removed from this stream for the purpose of recycling, as described in DE-A-102 004 004 683, filed at the same time as the present application.

SUMM According to embodiment IV, the process according to the invention is accordingly intended preferentially for mixtures which stem from a reaction of 1,3-butadiene with hydrogen cyanide over a hydrocyanation catalyst, or from an isomerization of 2-methyl-3-butenenitrile or from a reaction of 3-pentenenitrile with hydrogen cyanide over a hydrocyanation catalyst.

3. The process according to claim 1, wherein the mixture comprises 2-methyl-3-butenenitrile and 3-pentenenitrile and is produced from a reaction of 1,3-butadiene with hydrogen cyanide over a hydrocyanation catalyst.

7. The process according to claim 1, wherein the mixture comprises cis-2-pentenenitrile and 3-pentenenitrile and stems is produced from a reaction of 3-pentenenitrile with hydrogen cyanide over a hydrocyanation catalyst.

9. The process according to claim 1, wherein the mixture comprises (E)-2-methyl-2-butenenitrile and 3-pentenenitrile and is produced from a

reaction of 1,3-butadiene with hydrogen cyanide over a hydrocyanation catalyst or from the isomerization of 2-methyl-3-butenenitrile or from a reaction of 3-pentenenitrile with hydrogen cyanide over a hydrocyanation catalyst.

11. The process according to claim 2, wherein the mixture comprises 2-methyl-3-butenenitrile and 3-pentenenitrile and is produced from a reaction of 1,3-butadiene with hydrogen cyanide over a hydrocyanation catalyst.

13. The process according to claim 2 wherein the mixture comprises cis-2-pentenenitrile and 3-pentenenitrile and is produced from a reaction of 3-pentenenitrile with hydrogen cyanide over a hydrocyanation catalyst.

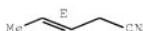
14. The process according to claim 2, wherein the mixture comprises (E)-2-methyl-2-butenenitrile and 3-pentenenitrile and is produced from a reaction of 1, 3-butadiene with hydrogen cyanide over a hydrocyanation catalyst or from the isomerization of 2-methyl-3-butenenitrile or from a reaction of 3-pentenenitrile with hydrogen cyanide over a hydrocyanation catalyst.

IT 4635-87-4P, 3-Pentenenitrile 16529-56-9P, 2-Methyl-3-butenenitrile 16529-66-1P, trans-3-Pentenenitrile 16545-78-1P, cis-3-Pentenenitrile 20068-02-4P, cis-2-Methyl-2-butenenitrile 25899-50-7P, cis-2-Pentenenitrile 27236-41-5P, Pentenenitrile 30574-97-1P, trans-2-Methyl-2-butenenitrile (vacuum distillation method for the separation of pentenenitrile isomers)
 IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,
 1,3-Butadiene, reactions
 (vacuum distillation method for the separation of pentenenitrile isomers prepared from)
 IT 4635-87-4P, 3-Pentenenitrile 16529-66-1P,
 trans-3-Pentenenitrile 16545-78-1P, cis-3-Pentenenitrile
 (vacuum distillation method for the separation of pentenenitrile isomers)
 RN 4635-87-4 USPATFULL
 CN 3-Pentenenitrile (CA INDEX NAME)



RN 16529-66-1 USPATFULL
 CN 3-Pentenenitrile, (3E)- (CA INDEX NAME)

Double bond geometry as shown.



RN 16545-78-1 USPATFULL
 CN 3-Pentenenitrile, (3Z)- (CA INDEX NAME)

Double bond geometry as shown.



IT 74-90-8 Hydrogen cyanide, reactions 106-99-0,
 1,3-Butadiene, reactions
 (vacuum distillation method for the separation of pentenenitrile isomers
 prepared
 from)
 RN 74-90-8 USPATFULL
 CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 USPATFULL
 CN 1,3-Butadiene (CA INDEX NAME)



L88 ANSWER 40 OF 60 USPATFULL on STN
 ACCESSION NUMBER: 2007:69511 USPATFULL Full-text
 TITLE: Sterically hindered chelate phosphinite-phosphite
 ligand, catalyst, comprising at least one nickel(0)
 complex stabilized by said ligand and method for
 production of nitriles
 INVENTOR(S): Bartsch, Michael, Neustadt, GERMANY, FEDERAL REPUBLIC
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 Jungkamp, Tim, Kapellen, BELGIUM
 Luyken, Hermann, Ludwigshafen, GERMANY, FEDERAL
 REPUBLIC OF
 Scheidel, Jens, Hirschberg, GERMANY, FEDERAL REPUBLIC
 OF
 Siegel, Wolfgang, Limburgerhof, GERMANY, FEDERAL
 REPUBLIC OF

| | NUMBER | KIND | DATE | |
|---------------------|-----------------|------|---------------|--------------|
| PATENT INFORMATION: | US 2007060766 | A1 | 20070315 | <-- |
| APPLICATION INFO.: | US 2004-577138 | A1 | 20041028 (10) | |
| | WO 2004-EP12176 | | 20041028 | |
| | | | 20060425 | PCT 371 date |

NUMBER DATE

PRIORITY INFORMATION: DE 2003-10350999 20031030
 DOCUMENT TYPE: Utility
 FILE SEGMENT: APPLICATION
 LEGAL REPRESENTATIVE: CONNOLLY BOVE LODGE & HUTZ LLP, P.O. BOX 2207,
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NUMBER OF CLAIMS: 20
 EXEMPLARY CLAIM: 1
 LINE COUNT: 744

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB The invention relates to phosphinite phosphites I of formula 1, 2, 3, 4, 5 or 6 and mixtures thereof, wherein R1, R2, R4 independently represent an alkyl or alkylene group with 1 to 8 carbon atoms, provided that at least one of the groups R1, R2, R4 is different from H; R5 to R22 independently represent H, an alkyl or alkylene group with 1 to 8 carbon atoms; R3 is H, methyl or ethyl; X is F, Cl or CF₃, if n=1 or 2 and X is H, if n=0.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

TI Sterically hindered chelate phosphinite-phosphite ligand, catalyst, comprising at least one nickel(0) complex stabilized by said ligand and method for production of nitriles

SUMM Catalyst comprising at least one nickel(0) complex stabilized by a sterically demanding chelate phosphinite phosphite ligand, and preparation of nitriles

SUMM . . . appropriate processes for their preparation. Moreover, the present invention relates to the use of the transition metal complexes as a catalyst and to processes in the presence of such transition metal complexes as a catalyst.

SUMM Chelate phosphinite phosphites, nickel complexes having such phosphinite phosphite ligands and the use of such complexes as a catalyst are known.

SUMM . . . It is desirable to improve the stability of the chelate phosphinite phosphite ligands to increase the on-stream time of the catalyst. Also desirable are an improvement in the selectivity of the catalyst, for example for 3-pentenenitrile in the hydrocyanation of butadiene or for adiponitrile in the hydrocyanation of 3-pentenenitrile, and an improvement. . .

SUMM . . . simple and economic manner, the hydrocyanation of unsaturated organic compounds with high stability, high reactivity and high selectivity of the catalyst.

SUMM The inventive transition metal complexes may be used as a catalyst, in particular as a homogeneous catalyst.

SUMM It has been found to be particularly advantageous to use the inventive transition metal complexes as a catalyst in the addition of hydrocyanic acid to olefinic double bonds, in particular those which are conjugated to a further olefinic. . . double bond, for example butadiene to obtain a mixture comprising 2-methyl-3-butenenitrile and 3-pentenenitrile. Equally advantageous is the use as a catalyst in the addition of hydrocyanic acid to olefinic double bonds which are not associated with a further olefinic double bond, . . .

SUMM It has likewise been found to be particularly advantageous to use the inventive transition metal complexes as a catalyst in the isomerization of organic nitriles, especially those in which the nitrile group is not conjugated to an olefinic double bond, for example 2-methyl-3-butenenitrile to obtain 3-pentenenitrile. Equally advantageous is also the use as a catalyst in the isomerization of organic nitriles in which the nitrile group is conjugated to an olefinic double bond.

SUMM . . . of monoolefinic C._{sub.5}-mononitriles having nonconjugated C.dbd.C and C.tbd.N bonds by hydrocyanating a 1,3-butadiene-containing hydrocarbon mixture in the presence of a catalyst, wherein the hydrocyanation is effected in the presence of at least one of the above-described inventive systems.

SUMM . . . under some circumstances, products are obtained in which a C.dbd.C double bond is conjugated with the C.tbd.N bond. "Applied Homogeneous Catalysis with Organometallic Compounds", Vol. 1, VCH Weinheim, p. 479 discloses that conjugated 2-pentenenitrile which is formed in the isomerization of . . . has been found that the abovementioned conjugated nitriles obtained in the hydrocyanation of an unpretreated C._{sub.4} cut also act as catalyst poisons for the first reaction step of adipic acid preparation, the monoaddition of hydrogen cyanide.

SUMM Therefore, those components which give rise to catalyst poisons in the course of catalytic hydrocyanation, especially alkynes, 1,2-dienes and mixtures thereof, are optionally partly or fully removed from the hydrocarbon mixture. To remove these components, the C._{sub.4} cut, before the addition of hydrogen cyanide, is preferably subjected to a catalytic partial hydrogenation. This partial hydrogenation is effected in the presence of a hydrogenation catalyst which is capable essentially of selectively hydrogenating alkynes and 1,2-dienes in addition to other dienes and monoolefins.

SUMM Suitable heterogeneous catalyst systems generally comprise a transition metal compound on an inert support. Suitable inorganic supports are the oxides which are customary for this purpose, in particular silicon oxides and aluminum oxides, aluminosilicates, zirconites, carbides, nitrides, etc., and mixtures thereof. The supports used are preferably Al._{sub.20}.sub.3, SiO._{sub.2} and mixtures thereof. They are in particular the heterogeneous catalysts used in U.S. Pat. No. 4,587,369; U.S. Pat. No. 4,704,492 and U.S. Pat. No. 4,493,906 which are fully incorporated here by way of reference. Further suitable Cu-based catalyst systems are sold by Dow Chemical as KLP catalyst.

SUMM . . .
a) charging a reactor with the hydrocarbon mixture, optionally a portion of the hydrogen cyanide and an inventive hydrocyanation catalyst which may optionally have been generated in situ, and also optionally a solvent,

b) reacting the mixture at elevated. . .

SUMM . . . reactor is charged before the start of the reaction with the part-hydrogenated C._{sub.4} cut or butadiene, hydrogen cyanide, a hydrocyanation catalyst and also optionally a solvent. Suitable solvents are the preferably aromatic hydrocarbons which have been mentioned above for the preparation of the inventive catalysts, such as toluene and xylene, or tetrahydrofuran.

SUMM . . . extracting, and the distillative workup of the remaining reaction mixture to remove the products of value and recover the still-active catalyst.

SUMM . . . 3-pentenenitrile and/or 4-pentenenitrile and a very small fraction of conjugated 2-pentenenitrile and 2-methyl-2-butenenitrile which are in some cases active as catalyst poison.

3. Preparation of adiponitrile by adding hydrogen cyanide to the 3-pentenenitrile formed in step 2 which has been. . .

SUMM The inventive catalysts based on phosphinite ligands are also advantageously suitable for the positional and double bond isomerization in step 2 and/or the. . .

SUMM Advantageously, the catalysts used in accordance with the invention do not only exhibit a high selectivity in relation to the monoaddition products obtained. . . of hydrogen cyanide in the hydrocyanation without noticeable deposition of inactive nickel(II) compounds, for

example nickel(II) cyanide. Unlike known hydrocyanation catalysts based on uncomplexed phosphine and phosphinite ligands, the catalysts containing a phosphinite phosphite I are thus suitable not only for continuous hydrocyanation processes in which a hydrogen cyanide excess . . . reaction mixture, but also for semicontinuous and batch processes in which there is generally a high hydrogen cyanide excess. The catalysts used in accordance with the invention and the processes for the hydrocyanation based on them thus generally have higher catalyst recycle rates and longer catalyst on-stream times than existing processes. In addition to better economic viability, this is also advantageous from the ecological viewpoint since the nickel cyanide formed from the active catalyst with hydrogen cyanide is highly poisonous and has to be worked up or disposed of at high cost.

SUMM The addition of hydrocyanic acid to an olefinic double bond in the presence of an inventive catalyst system, especially the addition to butadiene, a butadiene or to 3-pentenenitrile, 4-pentenenitrile or mixtures of such pentenenitriles, or the isomerization of organic nitriles in the presence of an inventive catalyst system, especially the isomerization of 2-methyl-3-butenenitrile to 3-pentenenitrile, may advantageously be carried out in the presence of one or more Lewis acids as promoters which influence the activity, selectivity or both of the inventive catalyst system. Useful promoters are inorganic and organic compounds in which the cation is selected from the group consisting of scandium, . . . group. U.S. Pat. No. 4,874,884 describes how synergistically active combinations of promoters, may be selected in order to increase the catalytic activity of the catalyst system. Preferred promoters include CdCl₂.sub.2, FeCl₂.sub.2, ZnCl₂.sub.2, B(C₂H₅.sub.5).sub.3 and (C₂H₅.sub.5).sub.3SnZ where Z is CF₃.sub.3SO₂.sub.3, CH₃.sub.3C₂H₅.sub.5H.sub.4SO₂.sub.3 or (C₂H₅.sub.5).sub.3BCN.

SUMM The molar ratio of promoter to nickel in the catalyst system may be between 1:16 and 50:1.

SUMM . . . by reference, with the proviso that an inventive system or a mixture of such systems is used instead of the catalysts specified in this patent specification.

SUMM . . . by reference, with the proviso that an inventive system or a mixture of such systems is used instead of the catalysts specified in this patent specification.

SUMM . . . by reference, with the proviso that an inventive system or a mixture of such systems is used instead of the catalysts specified in this patent specification.

SUMM . . . by reference, with the proviso that an inventive system or a mixture of such systems is used instead of the catalysts specified in this patent specification.

DETD All examples were carried out under a protective gas atmosphere of argon. The advantageous specification of the starting materials BD, HCN, 3PN and 2M3BN can be taken from WO 03/045552.

DETD In an argon atmosphere, 40 mmol of 2,2'-dihydroxy-3,3',5,5'-tetramethylbiphenol and 160 mmol of triethylamine are initially charged at -15° C. in 120 ml of. . .

DETD In an argon atmosphere, 40 mmol of 2,2'-dihydroxy-3,3',5,5',6,6'-hexamethylbiphenol and 160 mmol of triethylamine are initially charged at -15° C. in 120 ml of. . .

DETD In an argon atmosphere, 40 mmol of 2,2'-dihydroxy-3,3'-diisopropyl-6,6'-dimethylbiphenol and 44 mmol of diphenylchlorophosphine are initially charged at -15° C. in 120 ml of. . .

CLM What is claimed is:

7. The use of a transition metal complex as claimed in claim 4 as a catalyst.

10. A process comprising adding hydrocyanic acid to an olefinic double bond in the presence of a catalyst, wherein the catalyst is a transition metal complex as claimed in claim 5.
13. A process comprising isomerizing organic nitrites in the presence of a catalyst, wherein the catalyst used is a transition metal complex as claimed in claim 5.
- IT 74-90-8, Hydrocyanic acid, reactions 106-99-0,
1,3-Butadiene, reactions
(hydrocyanation; regioselective hydrocyanation of butadiene and unsatd. nitriles catalyzed by phosphinite-phosphite bidentate chelate nickel complexes in improved process for preparation of adiponitrile)
- IT 4635-87-4P, 3-Pentenenitrile
(isomerization, hydrocyanation; regioselective hydrocyanation of butadiene and unsatd. nitriles catalyzed by phosphinite-phosphite bidentate chelate nickel complexes in improved process for preparation of adiponitrile)
- TI Sterically hindered chelate phosphinite-phosphite ligand, catalyst, comprising at least one nickel(0) complex stabilized by said ligand and method for production of nitriles!
- PI US 2007060766 Al 20070315 <--|
- SUMM Catalyst comprising at least one nickel(0) complex stabilized by a sterically demanding chelate phosphinite phosphite ligand, and preparation of nitriles
- SUMM The present invention relates to novel phosphinite phosphites, in particular chelate phosphinite phosphites, and to a process for their preparation. The present invention further provides their use as a ligand in transition metal complexes, novel transition metal complexes and appropriate processes for their preparation. Moreover, the present invention relates to the use of the transition metal complexes as a catalyst and to processes in the presence of such transition metal complexes as a catalyst.
- SUMM Chelate phosphinite phosphites, nickel complexes having such phosphinite phosphite ligands and the use of such complexes as a catalyst are known.
- SUMM U.S. Pat. No. 5,693,843 and 5,523,453 describe processes for hydrocyanating unsaturated organic compounds and the isomerization of nitriles in the presence of nickel(0) complexes having chelate phosphinite phosphites as a ligand. It is desirable to improve the stability of the chelate phosphinite phosphite ligands to increase the on-stream time of the catalyst. Also desirable are an improvement in the selectivity of the catalyst, for example for 3-pentenenitrile in the hydrocyanation of butadiene or for adiponitrile in the hydrocyanation of 3-pentenenitrile, and an improvement in the space-time yield.
- SUMM It is an object of the present invention to provide phosphinite phosphites which are suitable as chelate phosphinite phosphites and enable, in a technically simple and economic manner, the hydrocyanation of unsaturated organic compounds with high stability, high reactivity and high selectivity of the catalyst.
- SUMM The inventive transition metal complexes may be used as a catalyst, in particular as a homogeneous catalyst.
- SUMM It has been found to be particularly advantageous to use the inventive

transition metal complexes as a catalyst in the addition of hydrocyanic acid to olefinic double bonds, in particular those which are conjugated to a further olefinic double bond, for example butadiene to obtain a mixture comprising 2-methyl-3-butenenitrile and 3-pentenenitrile. Equally advantageous is the use as a catalyst in the addition of hydrocyanic acid to olefinic double bonds which are not associated with a further olefinic double bond, for example 3-pentenenitrile or 4-pentenenitrile or mixtures thereof, preferably 3-pentenenitrile, to obtain adiponitrile, or 3-pentenoic ester or 4-pentenoic ester or mixtures thereof, preferably 3-pentenoic ester, to obtain 5-cyanovaleric ester.

SUMM It has likewise been found to be particularly advantageous to use the inventive transition metal complexes as a catalyst in the isomerization of organic nitriles, especially those in which the nitrile group is not conjugated to an olefinic double bond, for example 2-methyl-3-butenenitrile to obtain 3-pentenenitrile. Equally advantageous is also the use as a catalyst in the isomerization of organic nitriles in which the nitrile group is conjugated to an olefinic double bond.

SUMM The invention further provides a process for preparing mixtures of monoolefinic C._{sub.5}-mononitriles having nonconjugated C.dbd.C and C.tbd.N bonds by hydrocyanating a 1,3-butadiene-containing hydrocarbon mixture in the presence of a catalyst, wherein the hydrocyanation is effected in the presence of at least one of the above-described inventive systems.

SUMM C._{sub.4} cuts are optionally substantially freed of alkynes, e.g. propyne or butyne, of 1,2-dienes, e.g. propadiene, and of alkenynes, e.g. vinylacetylene. Otherwise, under some circumstances, products are obtained in which a C.dbd.C double bond is conjugated with the C.tbd.N bond. "Applied Homogeneous Catalysis with Organometallic Compounds", Vol. 1, VCH Weinheim, p. 479 discloses that conjugated 2-pentenenitrile which is formed in the isomerization of 2-methyl-3-butenenitrile and 3-pentenenitrile acts as a reaction inhibitor for the secondary addition of hydrogen cyanide to adiponitrile. It has been found that the abovementioned conjugated nitriles obtained in the hydrocyanation of an unpretreated C._{sub.4} cut also act as catalyst poisons for the first reaction step of adipic acid preparation, the monoaddition of hydrogen cyanide.

SUMM Therefore, those components which give rise to catalyst poisons in the course of catalytic hydrocyanation, especially alkynes, 1,2-dienes and mixtures thereof, are optionally partly or fully removed from the hydrocarbon mixture. To remove these components, the C._{sub.4} cut, before the addition of hydrogen cyanide, is preferably subjected to a catalytic partial hydrogenation. This partial hydrogenation is effected in the presence of a hydrogenation catalyst which is capable essentially of selectively hydrogenating alkynes and 1,2-dienes in addition to other dienes and monoolefins.

SUMM Suitable heterogeneous catalyst systems generally comprise a transition metal compound on an inert support. Suitable inorganic supports are the oxides which are customary for this purpose, in particular silicon oxides and aluminum oxides, aluminosilicates, zirconias, carbides, nitrides, etc., and mixtures thereof. The supports used are preferably Al._{sub.20}.sub.3, SiO_{sub.2} and mixtures thereof. They are in particular the heterogeneous catalysts used in U.S. Pat. No. 4,587,369; U.S. Pat. No. 4,704,492 and U.S. Pat. No. 4,493,906 which

are fully incorporated here by way of reference. Further suitable Cu-based catalyst systems are sold by Dow Chemical as KLP catalyst.

SUMM The semicontinuous process comprises:

- a) charging a reactor with the hydrocarbon mixture, optionally a portion of the hydrogen cyanide and an inventive hydrocyanation catalyst which may optionally have been generated in situ, and also optionally a solvent,
- b) reacting the mixture at elevated temperature and elevated pressure by feeding in hydrogen cyanide in semicontinuous mode in accordance with its consumption,
- c) completing the reaction by continued reaction and subsequent workup.

SUMM The pressure-rated reactor is charged before the start of the reaction with the part-hydrogenated C._{sub.4} cut or butadiene, hydrogen cyanide, a hydrocyanation catalyst and also optionally a solvent. Suitable solvents are the preferably aromatic hydrocarbons which have been mentioned above for the preparation of the inventive catalysts, such as toluene and xylene, or tetrahydrofuran.

SUMM To complete the conversion, the reaction time may be followed by a continued reaction time of from 0 minutes to about 5 hours, preferably from about 1 hour to 3.5 hours, in which no more hydrogen cyanide is fed into the autoclave. In this time, the temperature is left substantially constant at the reaction temperature set beforehand. The workup is effected by common methods and comprises the removal of the unconverted 1,3-butadiene and of the unconverted hydrogen cyanide, for example by washing or extracting, and the distillative workup of the remaining reaction mixture to remove the products of value and recover the still-active catalyst.

SUMM Generally, the preparation of adiponitrile from a butadiene-containing mixture by adding 2 molar equivalents of hydrogen cyanide can be divided into three steps:

1. Preparation of C._{sub.5} monoolefin mixtures having nitrile function.
2. Isomerization of the 2-methyl-3-butenenitrile present in these mixtures to 3-pentenenitrile and isomerization of the 3-pentenenitrile formed in this way and already present in the mixtures from step 1 to different n-pentenenitriles. This should form a very high fraction of 3-pentenenitrile and/or 4-pentenenitrile and a very small fraction of conjugated 2-pentenenitrile and 2-methyl-2-butenenitrile which are in some cases active as catalyst poison.
3. Preparation of adiponitrile by adding hydrogen cyanide to the 3-pentenenitrile formed in step 2 which has been isomerized beforehand in situ to 4-pentenenitrile. The by-products which occur are, for example, 2-methylglutarodinitrile from the Markovnikov addition of hydrogen cyanide to 4-pentenenitrile or the anti-Markovnikov addition of hydrogen cyanide to 3-pentenenitrile and ethylsuccinonitrile from the Markovnikov addition of hydrogen cyanide to 3-pentenenitrile.

SUMM The inventive catalysts based on phosphinite ligands are also advantageously suitable for the positional and double bond isomerization in step 2 and/or the secondary addition of hydrogen cyanide in step 3.

SUMM Advantageously, the catalysts used in accordance with the invention do not only exhibit a high selectivity in relation to the monoaddition products obtained in the hydrocyanation of 1,3-butadiene-containing hydrocarbon mixtures, but they may also be admixed with an excess of

hydrogen cyanide in the hydrocyanation without noticeable deposition of inactive nickel(II) compounds, for example nickel(II) cyanide. Unlike known hydrocyanation catalysts based on uncomplexed phosphine and phosphinite ligands, the catalysts containing a phosphinite phosphite I are thus suitable not only for continuous hydrocyanation processes in which a hydrogen cyanide excess is generally effectively avoided in the reaction mixture, but also for semicontinuous and batch processes in which there is generally a high hydrogen cyanide excess. The catalysts used in accordance with the invention and the processes for the hydrocyanation based on them thus generally have higher catalyst recycle rates and longer catalyst on-stream times than existing processes. In addition to better economic viability, this is also advantageous from the ecological viewpoint since the nickel cyanide formed from the active catalyst with hydrogen cyanide is highly poisonous and has to be worked up or disposed of at high cost.

- SUMM The addition of hydrocyanic acid to an olefinic double bond in the presence of an inventive catalyst system, especially the addition to butadiene, a butadiene or to 3-pentenenitrile, 4-pentenenitrile or mixtures of such pentenenitriles, or the isomerization of organic nitriles in the presence of an inventive catalyst system, especially the isomerization of 2-methyl-3-butenenitrile to 3-pentenenitrile, may advantageously be carried out in the presence of one or more Lewis acids as promoters which influence the activity, selectivity or both of the inventive catalyst system. Useful promoters are inorganic and organic compounds in which the cation is selected from the group consisting of scandium, titanium, vanadium, chromium, manganese, iron, cobalt, copper, zinc, boron, aluminum, yttrium, zirconium, niobium, molybdenum, cadmium, rhenium and tin. Examples include ZnBr₂, ZnI₂, ZnCl₂, ZnSO₄, CuCl₂, CuCl, Cu(O₂SCF₃)₂, CoCl₂, Col₂, FeI₂, FeCl₂, FeCl₂(THF), TiCl₄, TiCl₃, ClTi(0-iso-Pr)₂, MnCl₂, ScCl₃, AlCl₃, (C₂H₅AlCl)₂, (C₂H₅AlCl)₂I, (C₂H₅AlCl)₂SnCl₂, (C₂H₅AlCl)₂FeCl₂, (C₂H₅AlCl)₂YCl₃, (C₂H₅AlCl)₂Er(O₂SCF₃)₂, Yb(O₂CCF₃)₂, SmCl₃, B(C₂H₅AlCl)₂, TaCl₅, as generally described in U.S. Pat. No. 6,171,996 B1. Preferred promoters are also described in U.S. Pat. No. 3,496,217, U.S. Pat. No. 3,496,218 and U.S. Pat. No. 4,774,353. These include metal salts such as ZnCl₂, Col₂ and SnCl₂, and organometallic compounds such as RAlCl₂, R₂Sn₃O₂SCF₃, and R₂SnZ, where R is an alkyl group or aryl group. U.S. Pat. No. 4,874,884 describes how synergistically active combinations of promoters, may be selected in order to increase the catalytic activity of the catalyst system. Preferred promoters include CdCl₂, FeCl₂, ZnCl₂, B(C₂H₅AlCl)₂, (C₂H₅AlCl)₂SnZ where Z is CF₃SO₂, CH₂CH=CH₂, C₆H₅CO₂ or (C₂H₅AlCl)₂SCN.

SUMM The molar ratio of promoter to nickel in the catalyst system may be between 1:16 and 50:1.

SUMM A further advantageous embodiment of the hydrocyanation and isomerization can be taken from U.S. Pat. No. 5,981,772, whose contents are fully incorporated in the present application by reference, with the proviso that an inventive system or a mixture of such systems is used instead of the catalysts specified in this patent specification.

- SUMM A further advantageous embodiment of the hydrocyanation and isomerization can be taken from U.S. Pat. No. 6,127,567, whose contents are fully incorporated in the present application by reference, with the proviso that an inventive system or a mixture of such systems is used instead of the catalysts specified in this patent specification.
- SUMM A further advantageous embodiment of the hydrocyanation can be taken from U.S. Pat. No. 5,693,843, whose contents are fully incorporated in the present application by reference, with the proviso that an inventive system or a mixture of such systems is used instead of the catalysts specified in this patent specification.
- SUMM A further advantageous embodiment of the hydrocyanation can be taken from U.S. Pat. No. 5,523,453, whose contents are fully incorporated in the present application by reference, with the proviso that an inventive system or a mixture of such systems is used instead of the catalysts specified in this patent specification.
- DETD All examples were carried out under a protective gas atmosphere of argon. The advantageous specification of the starting materials BD, HCN, 3PN and 2M3BN can be taken from WO 03/045552.
- DETD In an argon atmosphere, 40 mmol of 2,2'-dihydroxy-3,3',5,5'-tetramethylbiphenol and 160 mmol of triethylamine are initially charged at -15° C. in 120 ml of toluene in a 500 ml flask. At this temperature, 44 mmol of diphenylchlorophosphine dissolved in 40 ml of toluene are added dropwise within 40 min. The mixture is stirred at -15° C. for a further 6 h. At -15° C., 40 mmol of di-o-cresyl chlorophosphite dissolved in 40 ml of toluene are added dropwise to the mixture. The mixture is allowed to come to room temperature and stirred for a further 15 h. The mixture is filtered and the filtrate fully concentrated. 25.3 g of product are obtained.
^{.sup.31P NMR} (C.sub.6D.sub.6): 133.5 ppm and 112.8 ppm; bisphosphinite impurities 112.5 ppm.
- DETD In an argon atmosphere, 40 mmol of 2,2'-dihydroxy-3,3',5,5',6,6'-hexamethylbiphenol and 160 mmol of triethylamine are initially charged at -15° C. in 120 ml of toluene in a 500 ml flask. At this temperature, 44 mmol of diphenylchlorophosphine dissolved in 40 ml of toluene are added dropwise within 40 min. The mixture is stirred at -15° C. for a further 6 h. At -15° C., 40 mmol of di-o-cresyl chlorophosphite dissolved in 40 ml of toluene are added dropwise to the mixture. The mixture is allowed to come to room temperature and stirred for a further 15 h. The mixture is filtered and the filtrate fully concentrated. 21.5 g of product are obtained.
^{.sup.31P NMR} (C.sub.6D.sub.6): 134.7 ppm and 110.6 ppm.
- DETD In an argon atmosphere, 40 mmol of 2,2'-dihydroxy-3,3'-diisopropyl-6,6'-dimethylbiphenol and 44 mmol of diphenylchlorophosphine are initially charged at -15° C. in 120 ml of toluene in a 500 ml flask. At this temperature, 160 mmol of triethylamine dissolved in 40 ml of toluene are added dropwise within 40 min. The mixture is stirred at -15° C. for a further 6 h. At -15° C., 40 mmol of di-o-cresyl chlorophosphite dissolved in 40 ml of toluene are added dropwise to the mixture. The mixture is allowed to come to room temperature and stirred for a further 15 h. The mixture is filtered and the filtrate fully concentrated. 21.5 g of product are obtained.
^{.sup.31P NMR} (C.sub.6D.sub.6): 132.5 ppm and 113.5 ppm.
7. The use of a transition metal complex as claimed in claim 4 as a catalyst.

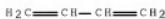
10. A process comprising adding hydrocyanic acid to an olefinic double bond in the presence of a catalyst, wherein the catalyst is a transition metal complex as claimed in claim 5.

13. A process comprising isomerizing organic nitrites in the presence of a catalyst, wherein the catalyst used is a transition metal complex as claimed in claim 5.

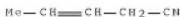
- IT 74-90-8, Hydrocyanic acid, reactions 106-99-0,
 1,3-Butadiene, reactions
 (hydrocyanation; regioselective hydrocyanation of butadiene and unsatd.
 nitriles catalyzed by phosphinite-phosphite bidentate chelate nickel
 complexes in improved process for preparation of adiponitrile)
- IT 4635-87-4P, 3-Pentenenitrile
 (isomerization, hydrocyanation; regioselective hydrocyanation of
 butadiene and unsatd. nitriles catalyzed by phosphinite-phosphite
 bidentate chelate nickel complexes in improved process for preparation of
 adiponitrile)
- IT 74-90-8, Hydrocyanic acid, reactions 106-99-0,
 1,3-Butadiene, reactions
 (hydrocyanation; regioselective hydrocyanation of butadiene and unsatd.
 nitriles catalyzed by phosphinite-phosphite bidentate chelate nickel
 complexes in improved process for preparation of adiponitrile)
- RN 74-90-8 USPATFULL
- CN Hydrocyanic acid (CA INDEX NAME)



- RN 106-99-0 USPATFULL
- CN 1,3-Butadiene (CA INDEX NAME)



- IT 4635-87-4P, 3-Pentenenitrile
 (isomerization, hydrocyanation; regioselective hydrocyanation of
 butadiene and unsatd. nitriles catalyzed by phosphinite-phosphite
 bidentate chelate nickel complexes in improved process for preparation of
 adiponitrile)
- RN 4635-87-4 USPATFULL
- CN 3-Pentenenitrile (CA INDEX NAME)



TITLE:

Process of synthesis of compounds having nitrile functions from ethylenically unsaturated compounds

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PATENT ASSIGNEE(S):

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| NUMBER | KIND | DATE |
|--------|------|------|
|--------|------|------|

PATENT INFORMATION:

US 2006252955 A1 20061109

APPLICATION INFO.:

US 2006-475210 A1 20060627 (11)

RELATED APPLN. INFO.:

Division of Ser. No. US 2003-353912, filed on 30 Jan 2003, GRANTED, Pat. No. US 7084293

| NUMBER | DATE |
|--------|------|
|--------|------|

PRIORITY INFORMATION:

FR 2002-16550 20021223

DOCUMENT TYPE:

Utility

FILE SEGMENT:

APPLICATION

LEGAL REPRESENTATIVE:

BUCHANAN, INGERSOLL & ROONEY PC, POST OFFICE BOX 1404, ALEXANDRIA, VA, 22313-1404, US

NUMBER OF CLAIMS:

24

EXEMPLARY CLAIM:

1

LINE COUNT:

699

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB A process of hydrocyanation of diolefins such as butadiene is carried out in the presence of a catalytic system comprising a transition metal and mono- and pluri-dentate organophosphorus ligands. The reaction medium containing branched nitrites subsequently is isomerized in the absence of hydrogen cyanide.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

DETD . . . the context of discontinuous performance, there can be charged into a reactor, purged beforehand with an inert gas (such as nitrogen, argon) either a solution containing the whole or a portion of the various constituents, such as the compound to undergo hydrocyanation, .

DETD If need be, a slight flushing of the reactor with an inert gas such as nitrogen or argon can be performed in order to expel the hydrogen cyanide which could still be present.

IT 74-90-6, Hydrogen cyanide, reactions 78-79-5, Isoprene, reactions 100-42-5, Styrene, reactions 106-99-0, Butadiene, reactions 110-59-8, Valeronitrile 110-83-8, Cyclohexene, reactions 111-69-3, Adiponitrile 111-78-4, 1,5-Cyclooctadiene 592-42-7, 1,5-Hexadiene 592-51-8, Pentene-4-nitrile 1335-86-0, Methylcyclohexene 4403-61-6, 2-Methyl-2-butenenitrile 4553-62-2, 2-Methyl glutaronitrile 4635-87-4, 3-Pentenenitrile 13284-42-9, 2-Pentenenitrile 16529-56-9, 2-Methyl-3-butenenitrile 17611-82-4, 2-Ethyl succinonitrile 25013-15-4, Methylstyrene 26588-32-9, Vinylnaphthalene

(process of synthesis of compds. having nitrile functions from ethylenically unsatd. compds. using organophosphorus ligand-metal complexes)

DETD In the context of discontinuous performance, there can be charged into a reactor, purged beforehand with an inert gas (such as nitrogen, argon) either a solution containing the whole or a portion of the various constituents, such as the compound to undergo hydrocyanation, the compounds of formulas (I) and (II), the transition metal compound, the possible reducing agent and solvent; or the said constituents

separately. The reactor is generally then brought to the chosen temperature. The hydrogen cyanide is then introduced, preferably in a continuous and regular manner.

DETD If need be, a slight flushing of the reactor with an inert gas such as nitrogen or argon can be performed in order to expel the hydrogen cyanide which could still be present.

IT 74-90-8, Hydrogen cyanide, reactions 78-79-5, Isoprene, reactions 100-42-5, Styrene, reactions 106-99-0, Butadiene, reactions 110-59-8, Valeronitrile 110-83-8, Cyclohexene, reactions 111-69-3, Adiponitrile 111-78-4, 1,5-Cyclooctadiene 592-42-7, 1,5-Hexadiene 592-51-8, Pentene-4-nitrile 1335-86-0, Methylcyclohexene 4403-61-6, 2-Methyl-2-butenenitrile 4553-62-2, 2-Methyl glutaronitrile 4635-87-4, 3-Pentenenitrile 13284-42-9, 2-Pentenenitrile 16529-56-9, 2-Methyl-3-butenenitrile 17611-82-4, 2-Ethyl succinonitrile 25013-15-4, Methylstyrene 26588-32-9, Vinylnaphthalene (process of synthesis of compds. having nitrile functions from ethylenically unsatd. compds. using organophosphorus ligand-metal complexes)

IT 74-90-8, Hydrogen cyanide, reactions 106-99-0, Butadiene, reactions 4635-87-4, 3-Pentenenitrile (process of synthesis of compds. having nitrile functions from ethylenically unsatd. compds. using organophosphorus ligand-metal complexes)

RN 74-90-8 USPATFULL

CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 USPATFULL

CN 1,3-Butadiene (CA INDEX NAME)



RN 4635-87-4 USPATFULL

CN 3-Pentenenitrile (CA INDEX NAME)



L88 ANSWER 42 OF 60 USPATFULL on STN

ACCESSION NUMBER: 2005:105739 USPATFULL Full-text

TITLE: Phosphonites, use thereof as ligand in transition metal complexes and method for production of nitriles

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 BASF Aktiengesellschaft, Ludwigshafen, GERMANY, FEDERAL
 REPUBLIC OF (non-U.S. corporation)

PATENT ASSIGNEE(S):

| | NUMBER | KIND | DATE | |
|---------------------|-----------------|------|----------|------|
| PATENT INFORMATION: | US 2005090678 | A1 | 20050428 | <-- |
| | US 7067685 | B2 | 20060627 | |
| APPLICATION INFO.: | US 2003-491918 | A1 | 20021004 | (10) |
| | WO 2002-EP11107 | | 20021004 | |

| | NUMBER | DATE |
|-----------------------|--|----------|
| PRIORITY INFORMATION: | DE 2001-10150281 | 20011012 |
| | DE 2003-10207165 | 20020220 |
| DOCUMENT TYPE: | Utility | |
| FILE SEGMENT: | APPLICATION | |
| LEGAL REPRESENTATIVE: | KEIL & WEINKAUF, 1350 CONNECTICUT AVENUE, N.W., WASHINGTON, DC, 20036, US | |
| NUMBER OF CLAIMS: | 14 | |
| EXEMPLARY CLAIM: | 1 | |
| LINE COUNT: | 786 | |

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB The invention relates to phosphinites I of formulae (1) or (2), in which R1, R2, R5, R6, R7, R8, R9 independently represent hydrogen, an alkyl or alkylene group having 1 to 8 carbon atoms or an alkoxy group having 1 to 8 carbon atoms; R3 is H or methyl; R4 is i-propyl or t-butyl; X is F, Cl or CF₃ and n is 1 or 2. ##STR1##

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

SUMM . . . use as ligands in transition metal complexes, novel transition metal complexes, a process for preparing the complexes, their use as catalyst and processes carried out in the presence of such transition metal complexes as catalyst.

SUMM Chelating phosphonites, nickel complexes containing such phosphonites as ligands and the use of such complexes as catalysts are known.

SUMM . . . It would be desirable to improve the stability of the chelating phosphonite ligands to increase the operating life of the catalyst. Furthermore, an improvement in the selectivity of the catalyst, for example to 3-pentenonitrile in the hydrocyanation of butadiene or to adiponitrile in the hydrocyanation of 3-pentenonitrile, and an improvement. . .

SUMM . . . provide phosphonites which are suitable as chelating phosphonites and display high stability, high reactivity and high selectivity when used as catalysts in the hydrocyanation of unsaturated organic compounds and make it possible for such hydrocyanations to be carried out in a. . .

SUMM . . . them, their use as ligands in transition metal complexes, novel transition metal complexes, processes for preparing them, their use as catalysts and processes carried out in the presence of such

transition metal complexes as catalysts.

SUMM The transition metal complexes of the present invention can be used as catalysts, in particular as homogeneous catalysts.

SUMM It has been found to be particularly advantageous to use the transition metal complexes of the present invention as catalysts in the addition of hydrocyanic acid onto olefinic double bonds, in particular double bonds which are conjugated with a further. . . a mixture comprising 2-methyl-3-butenenitrile and 3-pentenenitrile. It is equally advantageous to use the transition metal complexes of the invention as catalysts in the addition of hydrocyanic acid onto olefinic double bond which are not conjugated with a further olefinic double bond, . . .

SUMM It has likewise been found to be particularly advantageous to use the transition metal complexes of the present invention as catalysts in the isomerization of organic nitriles, in particular ones in which the nitrile group is not conjugated with an olefinic. . . of 2-methyl-3-butenenitrile to give 3-pentenenitrile. It is equally advantageous to use the transition metal complexes of the present invention as catalysts in the isomerization of organic nitriles in which the nitrile group is conjugated with an olefinic double bond.

SUMM . . . hydrocarbon mixture in the presence of at least one of the above described systems according to the present invention as catalyst.

SUMM . . . which a C.dbd.C double bond is conjugated with the C.dbd.N bond are sometimes obtained. It is known from "Applied Homogeneous Catalysis with Organometallic Compounds", vol. 1, VCH Weinheim, p. 479, that the conjugated 2-pentenenitrile formed in the isomerization of 2-methyl-3-butenenitrile and. . . has been found that the abovementioned conjugated nitriles obtained in the hydrocyanation of an unpretreated C.sub.4 fraction also act as catalyst poisons for the first reaction step of the preparation of adipic acid, namely the monoaddition of hydrogen cyanide.

SUMM For this reason, it may be useful to free the hydrocarbon mixture partly or completely of components which form catalyst poisons in the catalytic hydrocyanation, in particular alkynes, 1,2-dienes and mixtures thereof. To remove these components, the C.sub.4 fraction is subjected to a catalytic partial hydrogenation before the addition of hydrogen cyanide. This partial hydrogenation is carried out in the presence of a hydrogenation catalyst which is capable of selectively hydrogenating alkynes and 1,2-dienes in the presence of other dienes and monoolefins.

SUMM Suitable heterogeneous catalyst systems generally comprise a transition metal compound on an inert support. Suitable inorganic supports are the customary oxides, in particular silicon and aluminum oxides, aluminosilicates, zeolites, carbides, nitrides, etc., and mixtures thereof. Preference is given to using Al.sub.20.sub.3, SiO.sub.2 and mixtures thereof as supports. In particular, the heterogeneous catalysts used are those described in U.S. Pat. No. 4,587,369.; U.S. Pat. No. 4,704,492 and U.S. Pat. No. 4,493,906, which are hereby fully incorporated by reference. Further suitable catalyst systems based on Cu are marketed by Dow Chemical as KLP catalyst.

SUMM . . .

a) charging a reactor with the hydrocarbon mixture, if desired part of the hydrogen cyanide and a hydrocyanation catalyst according to the present invention, if desired produced in situ, and, if desired, a solvent,

b) reacting the mixture. . .

SUMM The pressure-rated reactor is charged with the partially hydrogenated C.sub.4 fraction or butadiene, hydrogen cyanide, a hydrocyanation catalyst and, if desired, a solvent prior to commencement of the

- reaction. Suitable solvents are those mentioned above for the preparation of the catalysts of the present invention, preferably aromatic hydrocarbons such as toluene and xylene, or tetrahydrofuran.
- SUMM . . . extraction, and fractionally distilling the remaining reaction mixture to separate off the products of value and recover the still active catalyst.
- SUMM . . . high proportion of 3-pentenenitrile or 4-pentenenitrile and a very small proportion of conjugated 2-pentenenitrile and 2-methyl-2-butenenitrile, which may act as catalyst poisons, should be formed.
- SUMM The novel catalysts based on phosphonite ligands can also be used advantageously for the structural isomerization and double bond isomerization in step 2. . .
- SUMM Advantageously, the catalysts used according to the present invention not only display a high selectivity to the monoaddition products obtained in the hydrocyanation. . . excess of hydrogen cyanide without appreciable deposition of inactive nickel(II) compounds, e.g. nickel(II) cyanide, occurring. In contrast to known hydrocyanation catalysts based on uncomplexed phosphine and phosphite ligands, the catalysts comprising a phosphonite I are thus suitable not only for continuous hydrocyanation processes in which an excess of hydrogen cyanide. . . but also for semicontinuous processes and batch processes in which a large excess of hydrogen cyanide is generally present. The catalysts used according to the present invention and the hydrocyanation processes based on them generally display higher catalyst recycle rates and longer catalyst operating times than do known processes. Apart from the economic aspect, this is also advantageous for ecological reasons since the nickel cyanide formed by reaction of the active catalyst with hydrogen cyanide is highly toxic and has to be worked up or disposed of at high cost.
- SUMM The addition of hydrocyanic acid onto an olefinic double bond in the presence of a catalyst system according to the present invention, in particular the addition onto butadiene or onto 3-pentenenitrile, 4-pentenenitrile or a mixture of such pentenenitriles or the isomerization of organic nitriles in the presence of a catalyst system according to the present invention, in particular the isomerization of 2-methyl-3-butenenitrile to 3-pentenenitrile, can advantageously be carried out in the presence of one or more Lewis acids as promoters which influence the activity, selectivity or both of the catalyst system of the present invention. Possible promoters are inorganic and organic compounds in which the cation is selected from the. . . group or aryl group. U.S. Pat. No. 4,874,884 describes the selection of synergistically effective combinations of promoters to increase the catalytic activity of the catalyst system. Preferred promoters include CdCl₂, FeCl₂, ZnCl₂, B(C₆H₅)₃.sub.3 and (C₆H₅)₂SnZ, where Z is CF₃.sub.3SO₃.sub.3, CH₃.sub.3C₆H₅.sub.3SO₃.sub.3 or (C₆H₅)₂BCN.
- SUMM The molar ratio of promoter to nickel in the catalyst system can be in the range from 1:16 to 50:1.
- SUMM . . . may be found in U.S. Pat. No. 5,981,772, whose contents are hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such catalyst systems is used in place of the catalysts mentioned in the patent cited.
- SUMM . . . may be found in U.S. Pat. No. 6,127,567, whose contents are hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such catalyst systems is used in place of the catalysts mentioned in the patent cited.
- SUMM . . . may be found in U.S. Pat. No. 5,693,843, whose contents are

hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such catalyst systems is used in place of the catalysts mentioned in the patent cited.

SUMM . . . may be found in U.S. Pat. No. 5,523,453, whose contents are hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such catalyst systems is used in place of the catalysts mentioned in the patent cited.

DETD All examples were carried out under a protective argon atmosphere.

DETD . . . this mixture and the mixture was stirred for a further 5 minutes. 94 equivalents of HCN/h⁺Ni in a stream of argon carrier gas were then introduced. Samples were taken from the reaction mixture after 30 minutes, 60 minutes and 150 minutes. . .

DETD . . . this mixture and the mixture was stirred for a further 5 minutes. 142 equivalents of HCN/h⁺Ni in a stream of argon carrier gas were then introduced. Samples were taken from the reaction mixture after 30 minutes and after 60 minutes and. . .

DETD . . . this mixture and the mixture was stirred for a further 5 minutes. 85 equivalents of HCN/h⁺Ni in a stream of argon carrier gas were then introduced. Samples were taken from the reaction mixture after 45 minutes and 60 minutes and analyzed. . .

DETD . . . to this mixture and the mixture was stirred for a further 5 minutes. 128 equivalents of HCN/h⁺Ni in a stream of argon carrier gas were then introduced. Samples were taken from the reaction mixture after 30 minutes and after 60 minutes and. . .

DETD . . . this mixture and the mixture was stirred for a further 5 minutes. 106 equivalents of HCN/h⁺Ni in a stream of argon carrier gas were then introduced. Samples were taken from the reaction mixture after 30 minutes and 60 minutes and analyzed. . .

DETD . . . this mixture and the mixture was stirred for a further 5 minutes. 123 equivalents of HCN/h⁺Ni in a stream of argon carrier gas were then introduced. Samples were taken from the reaction mixture after 30 minutes and 60 minutes and analyzed. . .

DETD . . . this mixture and the mixture was stirred for a further 5 minutes. 127 equivalents of HCN/h⁺Ni in a stream of argon carrier gas were then introduced. Samples were taken from the reaction mixture after 30 minutes and 60 minutes and analyzed. . .

DETD Virtually no temperature increase occurs. This means that the catalyst is not very active.

DETD Virtually no temperature increase occurs. This means that the catalyst is not very active.

CLM What is claimed is:

. . . them, their use as ligands in transition metal complexes, novel transition metal complexes, processes for preparing them, their use as catalysts and processes carried out in the presence of such transition metal complexes as catalysts.

7. The use of a transition metal complex as claimed in claim 4 or 5 as catalyst.

8. The use as claimed in claim 7 as catalyst for the addition of hydrocyanic acid onto an olefinic double bond.

9. The use as claimed in claim 7 as catalyst for the isomerization of organic nitriles.

. . . an olefinic double bond in the presence of a transition metal complex as claimed in claim 4 or 5 as catalyst.

- isomerization of organic nitrites in the presence of a transition metal complex as claimed in claim 4 or 5 as catalyst.
- IT 106-99-0, 1,3-Butadiene, reactions
 (hydrocyanation; use of phosphonites as cocatalysts in nickel complex catalyzed production of nitriles)
- IT 4635-87-4P, 3-Pentenenitrile
 (hydrocyanation; use of phosphonites as cocatalysts in nickel complex catalyzed production of nitriles)
- IT 592-51-8P, 4-Pentenenitrile 16529-66-1P, trans-3-Pentenenitrile
 16545-78-1P, cis-3-Pentenenitrile 20068-02-4P,
cis-2-Methyl-2-butenenitrile 26294-98-4P, trans-2-Pentenenitrile
 28906-50-5P, Methylglutaronitrile 30574-97-1P, trans-2-Methyl-2-butenenitrile
 (use of phosphonites as cocatalysts in nickel complex catalyzed production of nitriles)
- IT 74-90-8, Hydrogen cyanide, reactions
 (use of phosphonites as cocatalysts in nickel complex catalyzed production of nitriles)
- PI US 2005090678 A1 20050428 <-|||
 US 7067685 B2 20060627I
- SUMM** The present invention relates to novel phosphonites, in particular chelating phosphonites, methods of preparing them, their use as ligands in transition metal complexes, novel transition metal complexes, a process for preparing the complexes, their use as catalyst and processes carried out in the presence of such transition metal complexes as catalyst.
- SUMM** Chelating phosphonites, nickel complexes containing such phosphonites as ligands and the use of such complexes as catalysts are known.
- SUMM** WO 99/13983 and WO 99/64155 describe a process for the hydrocyanation of unsaturated organic compounds and the isomerization of nitriles in the presence of nickel(0) complexes containing chelating phosphonites as ligands. The chelating phosphonites described have good stability under the corresponding reaction conditions. It would be desirable to improve the stability of the chelating phosphonite ligands to increase the operating life of the catalyst. Furthermore, an improvement in the selectivity of the catalyst, for example to 3-pentenenitrile in the hydrocyanation of butadiene or to adiponitrile in the hydrocyanation of 3-pentenenitrile, and an improvement in the space-time yield are desirable.
- SUMM** It is an object of the present invention to provide phosphonites which are suitable as chelating phosphonites and display high, stability, high reactivity and high selectivity when used as catalysts in the hydrocyanation of unsaturated organic compounds and make it possible for such hydrocyanations to be carried out in a technically simple and economical manner.
- SUMM** We have found that this object is achieved by phosphonites I of the formula 1 or 2 ##STR2## where
- R1, R2, R5, R6, R7, R8, R9 are each, independently of one another, hydrogen, an alkyl or alkenylene group having from 1 to 8 carbon atoms or an alkoxy group having from 1 to 8 carbon atoms,
 R3 is H or methyl,
 R4 is i-propyl or t-butyl,
 X is F, Cl or CF₃,
 n is 1 or 2,

and also methods of preparing them, their use as ligands in transition metal complexes, novel transition metal complexes, processes for preparing them, their use as catalysts and processes carried out in the presence of such transition metal complexes as catalysts.

SUMM The transition metal complexes of the present invention can be used as catalysts, in particular as homogeneous catalysts.

SUMM It has been found to be particularly advantageous to use the transition metal complexes of the present invention as catalysts in the addition of hydrocyanic acid onto olefinic double bonds, in particular double bonds which are conjugated with a further olefinic double bond, for example onto a double bonds of butadiene to give a mixture comprising 2-methyl-3-butenenitrile and 3-pentenenitrile. It is equally advantageous to use the transition metal complexes of the invention as catalysts in the addition of hydrocyanic acid onto olefinic double bond which are not conjugated with a further olefinic double bond, for example onto the double bond of 3-pentenenitrile or 4-pentenenitrile or mixtures thereof, preferably 3-pentenenitrile, to give adiponitrile, or onto 3-pentenoic esters or 4-pentenoic esters or mixtures thereof, preferably 3-pentenoic esters, to give 5-cyanovaleric esters.

SUMM It has likewise been found to be particularly advantageous to use the transition metal complexes of the present invention as catalysts in the isomerization of organic nitriles, in particular ones in which the nitrile group is not conjugated with an olefinic double bond, for example the isomerization of 2-methyl-3-butenenitrile to give 3-pentenenitrile. It is equally advantageous to use the transition metal complexes of the present invention as catalysts in the isomerization of organic nitriles in which the nitrile group is conjugated with an olefinic double bond.

SUMM The invention also provides a process for preparing mixtures of monoolefinic C_{sub}.5-mononitriles having nonconjugated C_{dbd}.C and C_{dbd}.N bonds by hydrocyanation of a 1,3-butadiene-containing hydrocarbon mixture in the presence of at least one of the above described systems according to the present invention as catalyst.

SUMM C_{sub}.4 fractions are, if desired, substantially freed of alkynes, e.g. propyne or butyne, of 1,2-dienes, e.g. propadiene, and of alkenynes, e.g. vinylacetylene. Otherwise, products in which a C_{dbd}.C double bond is conjugated with the C_{dbd}.N bond are sometimes obtained. It is known from "Applied Homogeneous Catalysis with Organometallic Compounds", vol. 1, VCH Weinheim, p. 479, that the conjugated 2-pentenenitrile formed in the isomerization of 2-methyl-3-butenenitrile and 3-pentenenitrile acts as a reaction inhibitor for the second addition of hydrogen cyanide to form adiponitrile. It has been found that the abovementioned conjugated nitriles obtained in the hydrocyanation of an unpretreated C_{sub}.4 fraction also act as catalyst poisons for the first reaction step of the preparation of adipic acid, namely the monoaddition of hydrogen cyanide.

SUMM For this reason, it may be useful to free the hydrocarbon mixture partly or completely of components which form catalyst poisons in the catalytic hydrocyanation, in particular alkynes, 1,2-dienes and mixtures thereof. To remove these components, the C_{sub}.4 fraction is subjected to a catalytic partial hydrogenation before the addition of hydrogen cyanide. This partial hydrogenation is carried out in the presence of a hydrogenation catalyst which is capable of selectively hydrogenating alkynes and 1,2-dienes in the presence of other dienes and

monoolefins.

SUMM Suitable heterogeneous catalyst systems generally comprise a transition metal compound on an inert support. Suitable inorganic supports are the customary oxides, in particular silicon and aluminum oxides, aluminosilicates, zeolites, carbides, nitrides, etc., and mixtures thereof. Preference is given to using Al₂O₃, SiO₂ and mixtures thereof as supports. In particular, the heterogeneous catalysts used are those described in U.S. Pat. No. 4,587,369.; U.S. Pat. No. 4,704,492 and U.S. Pat. No. 4,493,906, which are hereby fully incorporated by reference. Further suitable catalyst systems based on Cu are marketed by Dow Chemical as KLP catalyst.

SUMM The semicontinuous process comprises:

- a) charging a reactor with the hydrocarbon mixture, if desired part of the hydrogen cyanide and a hydrocyanation catalyst according to the present invention, if desired produced in situ, and, if desired, a solvent,
- b) reacting the mixture at elevated temperature and superatmospheric pressure, with hydrogen cyanide being fed in at the rate at which it is consumed,
- c) completing the conversion by a period of after-reaction and subsequently working up the mixture.

SUMM The pressure-rated reactor is charged with the partially hydrogenated C₄ fraction or butadiene, hydrogen cyanide, a hydrocyanation catalyst and, if desired, a solvent prior to commencement of the reaction. Suitable solvents are those mentioned above for the preparation of the catalysts of the present invention, preferably aromatic hydrocarbons such as toluene and xylene, or tetrahydrofuran.

SUMM To complete the conversion, the reaction time can be followed by an after-reaction time of up to about 5 hours, preferably from about 1 hour to 3.5 hours, during which no more hydrogen cyanide is fed into the autoclave. During this time, the temperature is kept essentially constant at the reaction temperature set during the addition of hydrogen cyanide. Work-up is carried out by customary methods and comprises separating off the unreacted 1,3-butadiene and the unreacted hydrogen cyanide, e.g. by washing or extraction, and fractionally distilling the remaining reaction mixture to separate off the products of value and recover the still active catalyst.

SUMM 2. Isomerization of the 2-methyl-3-butenenitrile present in these mixtures to form 3-pentenenitrile and isomerization of the 3-pentenenitrile formed in this way and the 3-pentenenitrile already present in the mixtures from step 1 to form various n-pentenenitriles. A very high proportion of 3-pentenenitrile or 4-pentenenitrile and a very small proportion of conjugated 2-pentenenitrile and 2-methyl-2-butenenitrile, which may act as catalyst poisons, should be formed.

SUMM The novel catalysts based on phosphonite ligands can also be used advantageously for the structural isomerization and double bond isomerization in step 2 and/or the second addition of hydrogen cyanide in step 3.

SUMM Advantageously, the catalysts used according to the present invention not only display a high selectivity to the monoaddition products obtained in the hydrocyanation of 1,3-butadiene-containing hydrocarbon mixtures but they can also be admixed with an excess of hydrogen cyanide without appreciable deposition of inactive nickel(II) compounds, e.g.

nickel(II) cyanide, occurring. In contrast to known hydrocyanation catalysts based on uncomplexed phosphine and phosphite ligands, the catalyst comprising a phosphonite I are thus suitable not only for continuous hydrocyanation processes in which an excess of hydrogen cyanide in the reaction mixture can generally be effectively avoided but also for semicontinuous processes and batch processes in which a large excess of hydrogen cyanide is generally present. The catalysts used according to the present invention and the hydrocyanation processes based on them generally display higher catalyst recycle rates and longer catalyst operating times than do known processes. Apart from the economic aspect, this is also advantageous for ecological reasons since the nickel cyanide formed by reaction of the active catalyst with hydrogen cyanide is highly toxic and has to be worked up or disposed of at high cost.

SUMM The addition of hydrocyanic acid onto an olefinic double bond in the presence of a catalyst system according to the present invention, in particular the addition onto butadiene or onto 3-pentenenitrile, 4-pentenenitrile or a mixture of such pentenenitriles or the isomerization of organic nitriles in the presence of a catalyst system according to the present invention, in particular the isomerization of 2-methyl-3-butenenitrile to 3-pentenenitrile, can advantageously be carried out in the presence of one or more Lewis acids as promoters which influence the activity, selectivity or both of the catalyst system of the present invention. Possible promoters are inorganic and organic compounds in which the cation is selected from the group consisting of scandium, titanium, vanadium, chromium, manganese, iron, cobalt, copper, zinc, boron, aluminum, yttrium, zirconium, niobium, molybdenum, cadmium, rhenium and tin. Examples which may be mentioned are ZnBr.₂, ZnI.₂, ZnCl.₂, ZnSO.₄, CuCl.₂, CuCl, Cu(O.₂SCF₂).₂, CoCl.₂, CoI.₂, FeI.₂, FeCl.₃, FeCl.₂, FeCl.₂(THF).₂, TiCl.₄(THF).₂, TiCl.₄, TiCl.₃, TiCl(O-iso-Pr).₂, MnCl.₂, ScCl.₃, AlCl.₃, (C.₈H.₈Sn).AlCl.₂, (C.₈H.₈Sn).₂AlCl, (iso-C.₄H.₉).AlCl.₂, Ph.₂AlCl, PhAlCl.₂, ReCl.₅, ZrCl.₄, ZrCl.₂, NbCl.₅, VCl.₃, CrCl.₂, MoCl.₅, YCl.₃, CdCl.₂, LaCl.₃, Er(O.₂SCF₂).₃, sub.3, Yb(O.₂CCF₃).₃, SmCl.₃, B(C.₆H.₅).₂, TaCl.₅, as are generally described, for example in U.S. Pat. No. 6,171,996 B1. Further suitable promoters are described in the patents U.S. Pat. No. 3,496,217, U.S. Pat. No. 3,496,218 and U.S. Pat. No. 4,774,353. These comprise metal salts such as ZnCl.₂, CoI.₂ and SnCl.₂, and organometallic compounds such as RAICl.₂, R.₂SnO.₂SCF₃ and R.₂SnZ, where R is an alkyl group or aryl group. U.S. Pat. No. 4,874,884 describes the selection of synergistically effective combinations of promoters to increase the catalytic activity of the catalyst system. Preferred promoters include CdCl.₂, FeCl.₂, ZnCl.₂, B(C.₆H.₅).₂, (C.₈H.₈Sn).₂3SnZ, where Z is CF.₃SO.₂Z, CH.₂CH(C₆H₅)₂SO₂Z or (C.₆H.₅).₂BCN.

SUMM The molar ratio of promoter to nickel in the catalyst system can be in the range from 1:16 to 50:1.

SUMM A further advantageous embodiment of hydrocyanation and isomerization may be found in U.S. Pat. No. 5,981,772, whose contents are hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such catalyst systems is used in place of the catalysts mentioned in the patent cited.

SUMM A further advantageous embodiment of hydrocyanation may be found in U.S. Pat. No. 6,127,567, whose contents are hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such catalyst systems is used in place of the catalysts mentioned in the patent cited.

SUMM A further advantageous embodiment of hydrocyanation and isomerization may be found in U.S. Pat. No. 5,693,843, whose contents are hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such catalyst systems is used in place of the catalysts mentioned in the patent cited.

SUMM A further advantageous embodiment of hydrocyanation may be found in U.S. Pat. No. 5,523,453, whose contents are hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such catalyst systems is used in place of the catalysts mentioned in the patent cited.

DETD All examples were carried out under a protective argon atmosphere.
 DETD 1 equivalent of nickel(0)-(m-/p-tolyl phosphite) was admixed with 365 equivalents of 3PN, stirred at 25° C. for one hour and heated to 70° C. 1 equivalent of ZnCl₂.sub.2 was added to this mixture and the mixture was stirred for a further 5 minutes. 94 equivalents of HCN/h⁺Ni in a stream of argon carrier gas were then introduced. Samples were taken from the reaction mixture after 30 minutes, 60 minutes and 150 minutes and analyzed by gas chromatography (GC percent by weight, internal standard: ethylbenzene). The following results were obtained:

| Time | MGN | ADN | ADN selectivity (%) |
|---------|------|-------|---------------------|
| 30 min | 3.35 | 10.75 | 76.2 |
| 60 min | 6.87 | 26.39 | 79.3 |
| 150 min | 7.11 | 27.82 | 79.6 |

DETD 1 equivalent of Ni(COD)₂ was admixed with 3 equivalents of ligand 2 and 365 equivalents of 3PN, stirred at 25° C. for one hour and heated to 70° C. 1 equivalent of ZnCl₂.sub.2 was added to this mixture and the mixture was stirred for a further 5 minutes. 142 equivalents of HCN/h⁺Ni in a stream of argon carrier gas were then introduced. Samples were taken from the reaction mixture after 30 minutes and after 60 minutes and analyzed by gas chromatography (GC percent by weight, internal standard: ethylbenzene). The following results were obtained:

| Time | MGN | ADN | ADN selectivity (%) |
|--------|------|-------|---------------------|
| 30 min | 1.80 | 18.91 | 91.3 |
| 60 min | 2.51 | 32.57 | 92.9 |

DETD 1 equivalent of Ni(COD)₂ was admixed with 3 equivalents of ligand 1 and 365 equivalents of 3PN, stirred at 25° C. for one hour and heated to 70° C. 1 equivalent of ZnCl₂.sub.2 was added to this mixture and the mixture was stirred for a further 5 minutes. 85 equivalents of HCN/h⁺Ni in a stream of argon carrier gas were then introduced. Samples were taken from the reaction mixture after 45 minutes and 60 minutes and analyzed by gas chromatography (GC percent by weight, internal standard: ethylbenzene). The following results were

obtained:

| Time | MGN | ADN | ADN selectivity (%) |
|------|-----|-----|---------------------|
|------|-----|-----|---------------------|

| | | | |
|--------|------|-------|------|
| 45 min | 1.46 | 14.12 | 90.6 |
| 60 min | 1.92 | 21.60 | 91.8 |

DETD 1 equivalent of Ni(COD).sub.2 was admixed with 3 equivalents of ligand 3 and 365 equivalents of 3PN, stirred at 25° C. for one hour and heated to 70° C. 1 equivalent of ZnCl.sub.2 was added to this mixture and the mixture was stirred for a further 5 minutes. 128 equivalents of HCN/h⁺Ni in a stream of argon carrier gas were then introduced. Samples were taken from the reaction mixture after 30 minutes and after 60 minutes and analyzed by gas chromatography (GC percent by weight, internal standard: ethylbenzene). The following results were obtained:

| Time | MGN | ADN | ADN selectivity (%) |
|------|-----|-----|---------------------|
|------|-----|-----|---------------------|

| | | | |
|--------|------|-------|------|
| 30 min | 1.92 | 24.03 | 94.5 |
| 60 min | 1.93 | 38.05 | 95.2 |

DETD 1 equivalent of Ni(COD).sub.2 was admixed with 3 equivalents of ligand 4 and 365 equivalents of 3PN, stirred at 25° C. for one hour and heated to 70° C. 1 equivalent of ZnCl.sub.2 was added to this mixture and the mixture was stirred for a further 5 minutes. 106 equivalents of HCN/h⁺Ni in a stream of argon carrier gas were then introduced. Samples were taken from the reaction mixture after 30 minutes and 60 minutes and analyzed by gas chromatography (GC percent by weight, internal standard: ethylbenzene). The following results were obtained:

| Time | MGN | ADN | ADN selectivity (%) |
|------|-----|-----|---------------------|
|------|-----|-----|---------------------|

| | | | |
|--------|------|-------|------|
| 30 min | 1.32 | 16.61 | 92.6 |
| 60 min | 2.20 | 36.17 | 94.3 |

DETD 1 equivalent of Ni(COD).sub.2 was admixed with 3 equivalents of ligand 6 and 365 equivalents of 3PN, stirred at 25° C. for one hour and heated to 70° C. 1 equivalent of ZnCl.sub.2 was added to this mixture and the mixture was stirred for a further 5 minutes. 123 equivalents of HCN/h⁺Ni in a stream of argon carrier gas were then introduced. Samples were taken from the reaction mixture after 30 minutes and 60 minutes and analyzed by gas chromatography (GC percent by weight, internal standard: ethylbenzene). The following results were obtained:

| Time | MGN | ADN | ADN selectivity (%) |
|------|-----|-----|---------------------|
|------|-----|-----|---------------------|

| | | | |
|--------|------|-------|------|
| 30 min | 2.24 | 24.17 | 91.5 |
| 60 min | 3.57 | 46.91 | 92.9 |

DETD 1 equivalent of nickel(0)-(m-/p-tolyl phosphite) was admixed with 3 equivalents of ligand 6 and 365 equivalents of 3PN, stirred at 25° C. for one hour and heated to 70° C. 1 equivalent of ZnCl.sub.2 was added to this mixture and the mixture was stirred for a

further 5 minutes. 127 equivalents of HCN/h⁺Ni in a stream of argon carrier gas were then introduced. Samples were taken from the reaction mixture after 30 minutes and 60 minutes and analyzed by gas chromatography (GC percent by weight, internal standard: ethylbenzene). The following results were obtained:

| Time | MGN | ADN | ADN selectivity (%) |
|------|-----|-----|------------------------|
|------|-----|-----|------------------------|

| | | | |
|--------|------|-------|------|
| 30 min | 1.66 | 20.93 | 92.6 |
| 60 min | 2.74 | 32.36 | 92.2 |

DETD Virtually no temperature increase occurs. This means that the catalyst is not very active.

DETD Virtually no temperature increase occurs. This means that the catalyst is not very active.

1. A phosphonite I of the formula 1 or 2 ##STR4## where R₁, R₂, R₅, R₆, R₇, R₈, R₉ are each, independently of one another, hydrogen, an alkyl or alkylene group having from 1 to 8 carbon atoms or an alkoxy group having from 1 to 8 carbon atoms, R₃ is H or methyl, R₄ is i-propyl or t-butyl, X is F, Cl or CF_n where n is 1 or 2 and also methods of preparing them, their use as ligands in transition metal complexes, novel transition metal complexes, processes for preparing them, their use as catalysts and processes carried out in the presence of such transition metal complexes as catalysts.

7. The use of a transition metal complex as claimed in claim 4 or 5 as catalyst.

8. The use as claimed in claim 7 as catalyst for the addition of hydrocyanic acid onto an olefinic double bond.

9. The use as claimed in claim 7 as catalyst for the isomerization of organic nitriles.

10. A process for the addition of hydrocyanic acid onto an olefinic double bond in the presence of a transition metal complex as claimed in claim 4 or 5 as catalyst.

12. A process for the isomerization of organic nitriles in the presence of a transition metal complex as claimed in claim 4 or 5 as catalyst.

IT 106-99-0, 1,3-Butadiene, reactions
(hydrocyanation; use of phosphonites as cocatalysts in nickel complex catalyzed production of nitriles)

IT 4635-87-4P, 3-Pentenenitrile
(hydrocyanation; use of phosphonites as cocatalysts in nickel complex catalyzed production of nitriles)

IT 592-51-8P, 4-Pentenenitrile 16529-66-1P, trans-3-Pentenenitrile
16545-78-1P, cis-3-Pentenenitrile 20068-02-4P,
cis-2-Methyl-2-butenenitrile 26294-98-4P, trans-2-Pentenenitrile
28906-50-5P, Methylglutaronitrile 30574-97-1P, trans-2-Methyl-2-butenenitrile
(use of phosphonites as cocatalysts in nickel complex catalyzed production of nitriles)

IT 74-90-8, Hydrogen cyanide, reactions
(use of phosphonites as cocatalysts in nickel complex catalyzed production of nitriles)

IT 106-99-0, 1,3-Butadiene, reactions
(hydrocyanation; use of phosphonites as cocatalysts in nickel complex

10/586490

catalyzed production of nitriles)
RN 106-99-0 USPATFULL
CN 1,3-Butadiene (CA INDEX NAME)



IT 4635-87-4P, 3-Pentenenitrile
(hydrocyanation; use of phosphonites as cocatalysts in nickel complex
catalyzed production of nitriles)
RN 4635-87-4 USPATFULL
CN 3-Pentenenitrile (CA INDEX NAME)



IT 16529-66-1P, trans-3-Pentenenitrile 16545-78-1P,
cis-3-Pentenenitrile
(use of phosphonites as cocatalysts in nickel complex catalyzed production
of nitriles)
RN 16529-66-1 USPATFULL
CN 3-Pentenenitrile, (3E)- (CA INDEX NAME)

Double bond geometry as shown.



RN 16545-78-1 USPATFULL
CN 3-Pentenenitrile, (3Z)- (CA INDEX NAME)

Double bond geometry as shown.



IT 74-90-8, Hydrogen cyanide, reactions
(use of phosphonites as cocatalysts in nickel complex catalyzed production
of nitriles)
RN 74-90-8 USPATFULL
CN Hydrocyanic acid (CA INDEX NAME)



L88 ANSWER 43 OF 60 USPATFULL on STN

ACCESSION . . .

and an organic compound comprising at least one ethylenic unsaturation. This reaction is carried out in the presence of a catalytic system comprising a metal element chosen from the group consisting of nickel, platinum and palladium and an organophosphorus ligand, the . . .

AB . . . and an organic compound comprising at least one ethylenic unsaturation. This reaction is carried out in the presence of a catalytic system comprising a metal element chosen from the group consisting of nickel, platinum and palladium and an organophosphorus ligand, the . . .

SUMM [0006] These reactions are generally carried out in the liquid phase in the presence of a catalyst based on a metal, generally nickel, present in the form of a complex with an organic ligand. This reaction can be carried out in a homogeneous medium, the catalyst being soluble in the hydrocyanation medium, in particular in the olefin or the nitrites or in a third solvent. It can also be carried out with a medium exhibiting several liquid phases, the catalyst being soluble in one of the phases, more specifically in the phase formed by a polar third solvent, generally water, . . . the nitrites, at least at ambient temperature. The latter embodiment makes it possible to more easily extract and recover the catalyst and thus to obtain nitrile compounds comprising fewer impurities contributed by the catalyst.

SUMM [0007] These catalytic systems have been disclosed in numerous patents and several classes of ligands have been studied. The ligands are generally organophosphorus . . .

SUMM . . . No. 3,496,217, which discloses the synthesis of adiponitrile by reaction of hydrogen cyanide with butadiene in the presence of a catalyst based on nickel complexed with a ligand, such as triaryl phosphite. This reaction is carried out with catalysis in a single-phase medium.

SUMM . . . for the synthesis of adiponitrile by hydrocyanation of butadiene. The reaction is carried out in a two-phase liquid medium, the catalyst being present in an aqueous phase. This process makes it possible to recover the adiponitrile, devoid of catalyst and therefore of metal, in the organic phase. The catalyst disclosed is also a catalyst based on a metal, such as nickel, in combination with a ligand of the phosphine type. However, this ligand comprises sulphonate radicals, making it possible to render the catalyst soluble or dispersible in water.

SUMM [0010] Furthermore, it is also known to combine the nickel-based catalyst with promoters, such as Lewis acids, such as, for example, zinc chloride or triphenylborane, for the hydrocyanation of an unsaturated. . .

SUMM . . . Research is continually being undertaken to improve the performance of the synthesis of nitrites by hydrocyanation, either by developing novel catalytic systems or by modifying the reaction conditions and compositions of the hydrocyanation medium.

SUMM . . . makes it possible to obtain high yields of and high selectivities for linear nitrites and an improved stability of the catalytic system.

SUMM [0015] According to one characteristic of the invention, the reaction is carried out in the presence of a catalytic system comprising a metal element chosen from the group consisting of nickel, platinum and palladium and an organophosphorus ligand, the . . .

SUMM . . . miscible at the reaction temperature. The reaction is carried out in a nonhomogeneous or two-phase medium. In this embodiment, the catalytic system is advantageously soluble in the ionic liquid.

SUMM . . . of the hydrocyanated products and of the ionic liquid, in particular in order to make possible the extraction of the catalytic system. This is because the solvent of low polarity has the role of rendering the ionic liquid insoluble in the. . .

SUMM [0019] Whatever the embodiment, it is preferable for the catalytic system to be at least partially miscible in the ionic liquid. Advantageously, this miscibility can be obtained by the presence. . .

SUMM [0020] The catalytic systems suitable for the invention are those which preferably comprise the element nickel in the zero oxidation state or a . . . or more generally compounds comprising phosphorus capable of giving a coordination compound with transition metals and more particularly the abovementioned catalytic metals, in particular with nickel. These compounds can be mono-, bi- or polydentate and can exhibit a hydrophobic or hydrophilic. . .

SUMM [0021] Such catalytic systems and their preparation processes are disclosed, for example, in French Patents 2 338 253, 2 710 909, 2 711. . .

SUMM [0025] As is disclosed in the above-mentioned patents, the catalyst can be prepared before its introduction into the medium or *in situ*.

SUMM [0026] For this, use is preferably made of the compounds of the metals forming the catalytic element, such as nickel, which are added to a medium in which the organophosphorus ligand is also soluble. Such a medium can be the ionic liquid. The catalytic system thus formed is added to the hydrocyanation medium.

SUMM . . . at a temperature of less than 100° C. are preferred as they make possible better separation and extraction of the catalyst from the reaction medium in the case of a two-phase system.

SUMM [0047] The amount of ligand used to form the catalyst is chosen so that the number of moles of this compound with respect to 1 mol of transition metal is. . .

SUMM . . . batchwise implementation, it is in practice possible to charge to a reactor, purged beforehand using an inert gas (such as nitrogen or argon), either a solution comprising all or a portion of the various constituents, the transition metal compound, the possible reducing agents. . .

SUMM . . . mixture is withdrawn after cooling and the reaction products are isolated, for example by separation of the phase comprising the catalytic system and of the phase formed by the solvent of low or no polarity, the hydrocyanated products and those which. . .

SUMM . . . product to be hydrocyanated is an unsaturated compound comprising a nitrile functional group, it is advantageous to use, with the catalytic system, a cocatalyst comprising at least one Lewis acid.

SUMM . . . of linear dinitriles with respect to all the dinitriles formed, and/or to increase the activity and the lifetime of the catalyst.

SUMM [0071] In the context of this preferred alternative form, the catalytic system being already present for the reaction for the hydrocyanation of butadiene, it is sufficient to halt any introduction of. . .

SUMM . . . it is possible, if appropriate, to carry out a slight flushing of the reactor using an inert gas, such as nitrogen or argon, for example, in order to drive off the hydrocyanic acid which might still be present.

SUMM [0075] As for the process for the hydrocyanation of compounds comprising ethylenic unsaturation, the catalytic system used for the isomerization can be prepared before its introduction into the reaction region. It is also possible to prepare the catalytic system "in situ" by simple mixing of these various constituents. The amount of transition metal compound and more particularly of. . .

SUMM . . . unsaturated nitrites to dinitriles to be carried out with a reaction system in accordance with the invention or any other

catalytic system already known for this reaction.

DETD . . . 300 ml of distilled water. 61.62 g (0.215 mol) of lithium bis(trifluoromethylsulphonyl)amide are added and the mixture is stirred under argon for 72 hours at ambient temperature. A two-phase system is formed. After extraction with 250 ml of dichloromethane, the organic. . .

DETD . . . 300 ml of distilled water. 69.46 g (0.242 mol) of lithium bis(trifluoromethylsulphonyl)amide are added and the mixture is stirred under argon for 90 hours at ambient temperature. A two-phase system is formed. After extraction with 250 ml of dichloromethane, the organic. . .

DETD . . . g (0.199 mol) of 1-butyl-2,3-dimethylimidazolium chloride are dissolved in 150 ml of acetone. After vigorous stirring at ambient temperature under argon for 72 hours, the solution is filtered through celite and then concentrated. After chromatography on an alumina column (eluent: dichloromethane). . .

DETD [0110] The following are introduced successively and under argon into a glass tube:

DETD . . . 100°C. for 3 hours with head cooling. At the end of the reaction, the tubes are cooled in liquid nitrogen. A known amount of butylbenzene (approximately 40 mg, to act as chromatography internal standard) is added to the two-phase reaction. . .

DETD . . . with various salts are collated in Table II below. By way of comparison, a test was carried out with a catalyst based on nickel and on a ligand, triphenylphosphine, in single-phase medium.

TABLE II

| | | Mass | |
|------|---|--|---------|
| | DC (%) | YD (%) | YD. . . |
| DETD | [0120] | The following are introduced successively and under argon into a glass tube: | |
| CLM | What is claimed is: | | |
| | . . . by reaction between hydrogen cyanide and an organic compound having at least one ethylenic unsaturation in the presence of a catalyst comprising an element selected from the group consisting of nickel, platinum and palladium and an organophosphorus ligand, said process comprising. . . | | |
| | 40. The process according to claim 26, wherein the metal element of the catalyst is nickel in the 0 or 1 oxidation state. | | |
| IT | 106-99-0, 1,3-Butadiene, reactions (hydrocyanation substrate; process for manufacture of nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents) | | |
| IT | 592-51-8F, 4-Pentenenitrile 4635-87-4F, 3-Pentenenitrile (isomerization product and hydrocyanation substrate; process for manufacture of nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents) | | |
| IT | 74-90-8, Hydrogen cyanide, reactions (process for manufacture of nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents) | | |
| PI | US 2004260112 Al 20041223 | | <-- |
| AB | The present invention relates to the manufacture of nitrile compounds from unsaturated organic compounds by reaction with hydrogen cyanide. It relates more particularly to the manufacture of nitrile compounds of use in the synthesis of adiponitrile, an important chemical intermediate in the manufacture of major chemical compounds, such as hexamethylenediamine and ε-caprolactam. The invention provides a process for the manufacture of organic compounds comprising at least one nitrile functional group by carrying out a | | |

hydrocyanation reaction between hydrogen cyanide and an organic compound comprising at least one ethylenic unsaturation. This reaction is carried out in the presence of a catalytic system comprising a metal element chosen from the group consisting of nickel, platinum and palladium and an organophosphorus ligand, the reaction medium additionally comprising an ionic liquid in the liquid state at least at the temperature at which the hydrocyanation reaction is carried out.

SUMM [0006] These reactions are generally carried out in the liquid phase in the presence of a catalyst based on a metal, generally nickel, present in the form of a complex with an organic ligand. This reaction can be carried out in a homogeneous medium, the catalyst being soluble in the hydrocyanation medium, in particular in the olefin or the nitrites or in a third solvent. It can also be carried out with a medium exhibiting several liquid phases, the catalyst being soluble in one of the phases, more specifically in the phase formed by a polar third solvent, generally water, which phase is distinct from that formed by the olefin and the nitrites, at least at ambient temperature. The latter embodiment makes it possible to more easily extract and recover the catalyst and thus to obtain nitrile compounds comprising fewer impurities contributed by the catalyst.

SUMM [0007] These catalytic systems have been disclosed in numerous patents and several classes of ligands have been studied. The ligands are generally organophosphorus compounds, such as phosphites, phosphinites, phosphonites or phosphines. They can be monodentate or polydentate. In the case of processes in a two-phase medium, these organophosphorus ligands advantageously comprise one or more ionizable groups, such as sulphonate, phosphonate, carboxylate or ammonium groups, for example, to render them soluble in the polar phase.

SUMM [0008] Mention may be made, as example of the disclosure of these processes, of U.S. Pat. No. 3,496,217, which discloses the synthesis of adiponitrile by reaction of hydrogen cyanide with butadiene in the presence of a catalyst based on nickel complexed with a ligand, such as triaryl phosphite. This reaction is carried out with catalysis in a single-phase medium.

SUMM [0009] With regard to French Patent No. 2 338 253, it also discloses a process for the synthesis of adiponitrile by hydrocyanation of butadiene. The reaction is carried out in a two-phase liquid medium, the catalyst being present in an aqueous phase. This process makes it possible to recover the adiponitrile, devoid of catalyst and therefore of metal, in the organic phase. The catalyst disclosed is also a catalyst based on a metal, such as nickel, in combination with a ligand of the phosphine type. However, this ligand comprises sulphonate radicals, making it possible to render the catalyst soluble or dispersible in water.

SUMM [0010] Furthermore, it is also known to combine the nickel-based catalyst with promoters, such as Lewis acids, such as, for example, zinc chloride or triphenylborane, for the hydrocyanation of an unsaturated nitrile compound.

SUMM [0011] Research is continually being undertaken to improve the performance of the synthesis of nitrites by hydrocyanation, either by developing novel catalytic systems or by modifying the reaction conditions and compositions of the hydrocyanation medium.

SUMM [0013] One of the aims of the present invention is to provide a novel process for the manufacture of nitrites by hydrocyanation of an olefin

by reaction with hydrogen cyanide which makes it possible to obtain high yields of and high selectivities for linear nitrates and an improved stability of the catalytic system.

SUMM [0015] According to one characteristic of the invention, the reaction is carried out in the presence of a catalytic system comprising a metal element chosen from the group consisting of nickel, platinum and palladium and an organophosphorus ligand, the reaction medium additionally comprising an ionic liquid which is in the liquid state at least at the temperature at which the hydrocyanation reaction is carried out.

SUMM [0017] In a second embodiment, the ionic liquid and the compound to be hydrocyanated are immiscible or are only partially miscible at the reaction temperature. The reaction is carried out in a nonhomogeneous or two-phase medium. In this embodiment, the catalytic system is advantageously soluble in the ionic liquid.

SUMM [0018] In both these embodiments, it is possible to add a solvent of low polarity. This solvent of low polarity can be added from the beginning of the reaction but can also be used only after the end of the reaction, in order thus to promote the separation of the hydrocyanated products and of the ionic liquid, in particular in order to make possible the extraction of the catalytic system. This is because the solvent of low polarity has the role of rendering the ionic liquid insoluble in the phase composed of the said solvent, the unconverted olefin and the nitrile compounds formed.

SUMM [0019] Whatever the embodiment, it is preferable for the catalytic system to be at least partially miscible in the ionic liquid. Advantageously, this miscibility can be obtained by the presence of at least one ionizable group in the molecule of the organophosphorus ligand. Mention may be made, as ionizable groups, of groups of anionic type, such as sulphonate, phosphonate, phosphinate, carboxylate or sulphinate, or of cationic type, such as guanidinium, ammonium, pyridinium, imidazolium, phosphonium or sulphonium, for example. The number and the nature of these ionic groups are preferably chosen in order to render the ligand soluble in the ionic liquid. It can be advantageous for the nature of the ionizable group to be identical to that of the anion or of the cation associated with the ionic liquid.

SUMM [0020] The catalytic systems suitable for the invention are those which preferably comprise the element nickel in the zero oxidation state or a complex with organophosphorus ligands which can comprise several ionizable groups described above or more generally compounds comprising phosphorus capable of giving a coordination compound with transition metals and more particularly the abovementioned catalytic metals, in particular with nickel. These compounds can be mono-, bi- or polydentate and can exhibit a hydrophobic or hydrophilic nature. These compounds have been disclosed in numerous patents relating to the hydrocyanation of butadiene and belong to several classes, including in particular the organophosphites, organophosphonites, organophosphinites and organophosphines.

SUMM [0021] Such catalytic systems and their preparation processes are disclosed, for example, in French Patents 2 338 253, 2 710 909, 2 711 987, 2 739 378 and 2 778 915.

SUMM [0025] As is disclosed in the above-mentioned patents, the catalyst can be prepared before its introduction into the medium or in situ.

- SUMM [0026] For this, use is preferably made of the compounds of the metals forming the catalytic element, such as nickel, which are added to a medium in which the organophosphorus ligand is also soluble. Such a medium can be the ionic liquid. The catalytic system thus formed is added to the hydrocyanation medium.
- SUMM [0042] The ionic liquid, to be suitable for the process of the invention, must be in the liquid state at least at the temperature at which the hydrocyanation reaction is carried out. However, ionic liquids which are found in the liquid state at a temperature of less than 100° C. are preferred as they make possible better separation and extraction of the catalyst from the reaction medium in the case of a two-phase system.
- SUMM [0047] The amount of ligand used to form the catalyst is chosen so that the number of moles of this compound with respect to 1 mol of transition metal is between 0.5 and 50 and preferably between 2 and 10.
- SUMM [0052] In the context of a batchwise implementation, it is in practice possible to charge to a reactor, purged beforehand using an inert gas (such as nitrogen or argon), either a solution comprising all or a portion of the various constituents, the transition metal compound, the possible reducing agents and solvents, or the said constituents separately. Generally, the reactor is then brought to the chosen temperature and then the compound to be hydrocyanated is introduced. The hydrogen cyanide is then itself introduced, preferably continuously and unvaryingly.
- SUMM [0053] When the reaction is complete, the reaction mixture is withdrawn after cooling and the reaction products are isolated, for example by separation of the phase comprising the catalytic system and of the phase formed by the solvent of low or no polarity, the hydrocyanated products and those which have not been converted, in the case of a two-phase system. The products from the latter phase can be separated, for example by distillation. In the case of a single-phase system, other separation means can be employed, such as, for example, distillation or liquid/liquid extraction.
- SUMM [0054] In the case where the product to be hydrocyanated is an unsaturated compound comprising a nitrile functional group, it is advantageous to use, with the catalytic system, a cocatalyst comprising at least one Lewis acid.
- SUMM [0057] The Lewis acid used as cocatalyst makes it possible in particular, in the case of the hydrocyanation of aliphatic nitrites comprising ethylenic unsaturation, to improve the linearity of the dinitriles obtained, that is to say the percentage of linear dinitriles with respect to all the dinitriles formed, and/or to increase the activity and the lifetime of the catalyst.
- SUMM [0071] In the context of this preferred alternative form, the catalytic system being already present for the reaction for the hydrocyanation of butadiene, it is sufficient to halt any introduction of hydrogen cyanide to allow the isomerization reaction to take place.
- SUMM [0072] In this alternative form, it is possible, if appropriate, to carry out a slight flushing of the reactor using an inert gas, such as nitrogen or argon, for example, in order to drive off the hydrocyanic acid which might still be present.

SUMM [0075] As for the process for the hydrocyanation of compounds comprising ethylenic unsaturation, the catalytic system used for the isomerization can be prepared before its introduction into the reaction region. It is also possible to prepare the catalytic system "in situ" by simple mixing of these various constituents. The amount of transition metal compound and more particularly of nickel compound used and the amount of ligand are the same as for the hydrocyanation reaction.

SUMM [0076] However, the preparation of dinitrile compounds by hydrocyanation of an olefin such as butadiene can be carried out using a reaction system in accordance with the invention for the stages of formation of the unsaturated nitrites and the stage of isomerization above, it being possible for the reaction for the hydrocyanation of the unsaturated nitrites to dinitriles to be carried out with a reaction system in accordance with the invention or any other catalytic system already known for this reaction.

DETD [0081] 40.50 g (0.215 mol) of 1-butyl-2,3-dimethylimidazolium chloride are dissolved in 300 ml of distilled water. 61.62 g (0.215 mol) of lithium bis(trifluoromethylsulphonyl)amide are added and the mixture is stirred under argon for 72 hours at ambient temperature. A two-phase system is formed. After extraction with 250 ml of dichloromethane, the organic phase is washed with 800 ml of water and then concentrated. The compound exists in the form of a slightly pinkish liquid which is purified by chromatography on a neutral alumina column (eluent: dichloromethane). It is then concentrated, taken up in acetonitrile in the presence of active carbon and filtered. After drying for several hours at 60° C., the compound is obtained in the form of a colourless liquid (83.78 g, 90%). The structure of this product, C₁₁H₂₂N₂, is confirmed by NMR spectral analysis.

DETD [0083] 41.92 g (0.240 mol) of 1-butyl-3-methylimidazolium chloride are dissolved in 300 ml of distilled water. 69.46 g (0.242 mol) of lithium bis(trifluoromethylsulphonyl)amide are added and the mixture is stirred under argon for 90 hours at ambient temperature. A two-phase system is formed. After extraction with 250 ml of dichloromethane, the organic phase is washed with 800 ml of water and then concentrated. The compound exists in the form of a slightly pinkish liquid which is purified by chromatography on a neutral alumina column (eluent: dichloromethane). It is then concentrated, taken up in acetonitrile in the presence of active carbon and filtered. After drying for several hours at 60° C., the compound is obtained in the form of a colourless liquid (81.47 g). Its structure, C₁₁H₂₂N₂, is confirmed by NMR analysis.

DETD [0085] 33.37 g (0.200 mol) of sodium hexafluorophosphate and 37.50 g (0.199 mol) of 1-butyl-2,3-dimethylimidazolium chloride are dissolved in 150 ml of acetone. After vigorous stirring at ambient temperature under argon for 72 hours, the solution is filtered through celite and then concentrated. After chromatography on an alumina column (eluent: dichloromethane), the salt is taken up in acetonitrile in the presence of active carbon and filtered. Concentrating the solution gives 50.41 g (0.170 mol, 85%) of a white solid. The structure of this product, C₁₁H₂₂N₂, is confirmed by NMR spectral analysis.

DETD [0110] The following are introduced successively and under argon into a glass tube:

DETD [0115] The tube is closed, then stirred and heated at 100° C. for 3 hours with head cooling. At the end of the reaction, the tubes are cooled in liquid nitrogen. A known amount of butylbenzene (approximately 40 mg, to act as chromatography internal standard) is

added to the two-phase reaction medium, which is diluted and homogenized by the addition of 10 ml of THF. The solution obtained is filtered through a short silica column and injected in gas chromatography (GC).

DETD [0117] The results obtained with various salts are collated in Table II below. By way of comparison, a test was carried out with a catalyst based on nickel and on a ligand, triphenylphosphine, in a single-phase medium.

TABLE II

| Ex. Salt | DC (%) 2M3BN | YD (%) 3PN + 4PN | YD (%) 2M2BN | YD (%) 2PN | Mass balance (%) |
|--|-----------------|---------------------|-----------------|---------------|------------------------|
| A (1) | 42 | 57 | -3.1 | 5.8 | 86 |
| 1 [BMI] [TF ₂ N] 95 | 95 | 90 | 2.9 | -0.4 | 96 |
| 2 [BMMI] [PF ₂ Sb ₂] 93 | 93 | 90 | 0.2 | 2.3 | 94 |
| 3 [BMMI] [TF ₂ N] | 96 | 94 | 0.8 | 1.6 | 98 |

(1) comparative test without ionic liquid with triphenylphosphine as ligand
DETD [0120] The following are introduced successively and under argon into a glass tube:

26. A process for the manufacture of organic compounds comprising at least one nitrile functional group by reaction between hydrogen cyanide and an organic compound having at least one ethylenic unsaturation in the presence of a catalyst comprising an element selected from the group consisting of nickel, platinum and palladium and an organophosphorus ligand, said process comprising the step of carrying out said reaction in a reaction medium with the presence of an ionic liquid which comprises at least one cation and at least one anion and which is liquid at least at a temperature at which the reaction is carried out.

40. The process according to claim 26, wherein the metal element of the catalyst is nickel in the 0 or 1 oxidation state.

- IT 106-99-0, 1,3-Butadiene, reactions
(hydrocyanation substrate; process for manufacture of nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents)
- IT 592-51-8P, 4-Pentenenitrile 4635-87-4P, 3-Pentenenitrile
(isomerization product and hydrocyanation substrate; process for manufacture of nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents)
- IT 74-90-8, Hydrogen cyanide, reactions
(process for manufacture of nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents)
- IT 106-99-0, 1,3-Butadiene, reactions
(hydrocyanation substrate; process for manufacture of nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid solvents)
- RN 106-99-0 USPATFULL
CN 1,3-Butadiene (CA INDEX NAME)



IT 4635-87-4P, 3-Pentenenitrile
 (isomerization product and hydrocyanation substrate; process for
 manufacture
 of nitriles by hydrocyanation of unsatd. compds. with HCN in ionic liquid
 solvents)
 RN 4635-87-4 USPATFULL
 CN 3-Pentenenitrile (CA INDEX NAME)



IT 74-90-8, Hydrogen cyanide, reactions
 (process for manufacture of nitriles by hydrocyanation of unsatd. compds.
 with HCN in ionic liquid solvents)
 RN 74-90-8 USPATFULL
 CN Hydrocyanic acid (CA INDEX NAME)



L88 ANSWER 44 OF 60 USPATFULL on STN
 ACCESSION NUMBER: 2004228236 USPATFULL Full-text
 TITLE: Catalyst system containing ni(0) for hydrocyanation
 INVENTOR(S): Bartsch, Michael, Neustadt, GERMANY, FEDERAL REPUBLIC
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 REPUBLIC OF

| | NUMBER | KIND | DATE | |
|---------------------|----------------|------|---------------|-----|
| PATENT INFORMATION: | US 2004176622 | A1 | 20040909 | <-- |
| APPLICATION INFO.: | US 2004-484169 | A1 | 20040120 (10) | |
| | WO 2002-EF7888 | | 20020716 | |

| | NUMBER | DATE |
|-----------------------|--|----------|
| PRIORITY INFORMATION: | DE 2001-10136488 | 20010727 |
| DOCUMENT TYPE: | Utility | |
| FILE SEGMENT: | APPLICATION | |
| LEGAL REPRESENTATIVE: | KEIL & WEINKAUF, 1350 CONNECTICUT AVENUE, N.W., WASHINGTON, DC, 20036 | |
| NUMBER OF CLAIMS: | 21 | |
| EXEMPLARY CLAIM: | 1 | |
| LINE COUNT: | 1060 | |

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB A catalyst system containing a) Ni (0), b) 4-10 mol per mol Ni (0) according to a) a compound (I) of formula P (X.sup.1R.sup.1) (X.sup.2R.sup.2) (X.sup.3R.sup.3) (I) wherein X.sup.1, X.sup.2, X.sup.3 independently represent oxygen or a single bond R.sup.1, R.sup.2, R.sup.3 represent independently, the same or different organic radicals, and c) 1-4 mol per mol Ni (0) according to a) a compound (II) of formula (II) wherein X.sup.11, X.sup.12, X.sup.13, X.sup.21, X.sup.22, X.sup.23 independently represent oxygen or a single bond, R.sup.11, R.sup.12 independently represent the same or different individual or bridged organic radicals, Y represents a bridge group. The invention also relates to a method for the production of mixtures of monoolefin C.sub.5-mononitriles with a n-conjugated C.dbd.C and C.dbd.N bond by hydrocyanation of a hydrocarbon mixture containing 1,3-butadiene in the presence of at least one such system and to a method for the production of a dinitrile by hydrocyanation of a mixture of monoolefin C.sub.5-mononitriles with a non-conjugated C.dbd.C-- and C.dbd.N bond in the presence of at least one such system. ##STR1##

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

TI Catalyst system containing ni(0) for hydrocyanation
 AB A catalyst system containing a) Ni (0), b) 4-10 mol per mol Ni (0) according to a) a compound (I) of formula . . .
 SUMM [0015] which is suitable as catalyst and to processes for preparing such systems.
 SUMM [0016] Systems comprising Ni(0) and a compound (II) which are suitable as catalysts for the hydrocyanation of butadiene to form a mixture of isomeric pentenenitriles and of pentenenitrile to form adiponitrile and processes. . .
 SUMM [0017] The preparation of these catalyst systems is technically complicated and expensive. This applies particularly since the catalyst systems are gradually decomposed during use and thus have to be discharged and replaced by fresh catalyst.
 SUMM . . . nickel as Ni(0) source with compound (II) in the presence or absence of a liquid diluent or hydrogen halide as catalyst leads to a large extent to decomposition of compound (II).
 SUMM . . . chloride and zinc as Ni(0) source is known. A disadvantage of this process is the simultaneous formation of the specified catalyst system and zinc chloride.
 SUMM [0022] If the use of the pure catalyst system is envisaged, the zinc chloride firstly has to be removed before use, which is costly.
 SUMM [0023] If the mixture of catalyst system and zinc chloride is used instead of the pure catalyst system, then the work-up of the mixture of exhausted catalyst system and zinc chloride poses a great problem.
 SUMM [0024] A further disadvantage of the catalyst system comprising Ni(0) and compound (II) is that compound (II) can be obtained only by way of a technically complicated. . .
 SUMM [0025] It is an object of the present invention to provide a catalyst system which can be synthesized in a technically simple and economical way and displays selectivities and activities comparable to those of a catalyst system comprising Ni(0) and compound (II), especially in the hydrocyanation of compounds having conjugated olefinic double bonds, e.g. butadiene, and. . .
 SUMM . . . first system in step a) can advantageously be carried out in the presence of a homogeneous or heterogeneous, preferably homogeneous, catalyst.
 SUMM [0092] As homogeneous catalyst, it is advantageous to use a protic acid or a mixture of such protic acids, for example hydrochloric acid.
 SUMM [0093] An advantageous homogeneous catalyst is a compound of the formula

- SUMM [0095] The catalyst used in step a) can be carried over from step a) to step b). It has been found to be advantageous to remove the catalyst from step a) between steps a) and b).
- SUMM . . . monoolefinic C.sub.5-mononitriles having nonconjugated C.dbd.C and C.dbd.N bonds by hydrocyanation of a 1,3-butadiene-containing hydrocarbon mixture in the presence of a catalyst comprising at least one of the above-described systems according to the present invention.
- SUMM . . . which a C.dbd.C double bond is conjugated with the C.dbd.N bond may be obtained. It is known from "Applied Homogeneous Catalysis with Organometallic Compounds", vol. 1, V. C. H. Weinheim, p. 479, that the conjugated 2-pentenenitrile formed in the isomerization of . . . has been found that the abovementioned conjugated nitriles obtained in the hydrocyanation of an unpretreated C.sub.4 fraction also act as catalyst poisons for the first reaction step of the production of adipic acid, viz. the monoaddition of hydrogen cyanide.
- SUMM [0105] For this reason, those components which act as catalyst poisons in catalytic hydrocyanation, in particular alkynes, 1,2-dienes and mixtures thereof, are advantageously removed completely or partially from the hydrocarbon mixture. To remove these components, the C.sub.4 fraction is subjected to a catalytic partial hydrogenation prior to the addition of hydrogen cyanide. This partial hydrogenation is carried out in the presence of a hydrogenation catalyst which is capable of selectively hydrogenating alkynes and 1,2-dienes in the presence of other dienes and monoolefins.
- SUMM [0106] Suitable heterogeneous catalyst systems generally comprise a transition metal compound on an inert support. Suitable inorganic supports are the oxides, in particular silicon and aluminum oxides, aluminosilicates, zeolites, carbides, nitrides, etc., customary for this purpose and mixtures thereof. Preferred supports are Al.sub.20.20.3, SiO.sub.2 and mixtures thereof. In particular, the heterogeneous catalysts used are those described in U.S. Pat. No. 4,587,369; U.S. Pat. No. 4,704,492 and U.S. Pat. No. 4,493,906, which are hereby fully incorporated by reference. Further suitable catalyst systems based on Cu are marketed by Dow Chemical as KLP catalyst.
- SUMM [0111] a) charging a reactor with the hydrocarbon mixture, if desired part of the hydrogen cyanide and a hydrocyanation catalyst according to the present invention, if desired one produced *in situ*, and, if desired, a solvent,
- SUMM [0116] The pressure-rated reactor is charged with the partially hydrogenated C.sub.4 fraction, hydrogen cyanide, a hydrocyanation catalyst and, if desired, a solvent prior to commencement of the reaction. Suitable solvents are those mentioned above for the preparation of the catalysts of the present invention, preferably aromatic hydrocarbons such as toluene and xylene or tetrahydrofuran.
- SUMM . . . working up the remaining reaction mixture by distillation to separate off the desired product and to recover the still active catalyst.
- SUMM . . . high proportion of 3-pentenenitrile or 4-pentenenitrile and a very low proportion of conjugated 2-pentenenitrile and 2-methyl-2-butenenitrile, which may act as catalyst poisons, should be formed.
- SUMM [0126] Advantageously, the catalysts of the present invention based on phosphonite ligands are also suitable for the structural isomerization and double bond isomerization in. . .
- SUMM [0128] Advantageously, the catalysts used according to the present invention not only display a high selectivity to the monoaddition products obtained in the hydrocyanation. . . cyanide in the hydrocyanation without appreciable precipitation of inactive nickel(II) compounds, e.g. nickel(II) cyanide, occurring. In contrast to known hydrocyanation catalysts based on uncomplexed phosphine and phosphite

ligands, the catalysts of the formula I are thus suitable not only for continuous hydrocyanation processes in which an excess of hydrogen cyanide. . . also for semicontinuous processes and batch processes in which a large excess of hydrogen cyanide is generally present. Thus, the catalysts used according to the present invention and the hydrocyanation processes based on them generally allow greater recirculation of catalysts and display longer catalyst operating lives than do known processes. This is advantageous both in terms of improved economics and also from an ecological point of view, since the nickel cyanide formed from the active catalyst by reaction with hydrogen cyanide is highly toxic and has to be worked up or disposed of, which is very. . .

SUMM . . . can be derived from U.S. Pat. No. 6,981,772, whose contents are hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such systems is used in place of the catalysts mentioned in that patent.

SUMM . . . can be derived from U.S. Pat. No. 6,127,567, whose contents are hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such systems is used in place of the catalysts mentioned in that patent.

SUMM . . . can be derived from U.S. Pat. No. 5,693,843, whose contents are hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such systems is used in place of the catalysts mentioned in that patent.

SUMM . . . can be derived from U.S. Pat. No. 5,523,453, whose contents are hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such systems is used in place of the catalysts mentioned in that patent.

DETD [0136] All examples were carried out under a protective argon atmosphere.

DETD . . . to this mixture and the mixture was stirred for a further 5 minutes. 94 molar equivalents of HCN/hour*Ni in an argon carrier gas stream were passed in. Samples were taken after 30 minutes, 60 minutes and 150 minutes and the following. . .

DETD . . . to this mixture and the mixture was stirred for a further 5 minutes. 133 molar equivalents of HCN/hour*Ni in an argon carrier gas stream were passed in.

DETD [0158] The procedure of Example 10 was repeated (using 0.58 mmol of Ni(0)), except that the catalyst mixture was stirred at 25° C. for 12 hours instead of 1 hour and 122 molar equivalents of HCN/h*Ni were. . .

CLM What is claimed is:

- · · R.sup.1, R.sup.2, R.sup.3 are each, independently of one another, a phenyl, o-tolyl, m-tolyl or p-tolyl group, which is suitable as catalyst.

- · · to 9, wherein the preparation of the first system in step a) is carried out in the presence of a catalyst.

- · · 9, wherein the preparation of the first system in step a) is carried out in the presence of a homogeneous catalyst.

- · · preparation of the first system in step a) is carried out in the presence of a protic acid as homogeneous catalyst.

- · · the preparation of the first system in step a) is carried out in the presence of hydrogen chloride as homogeneous catalyst.

- · · (R.sup.1X.sup.1)(R.sup.2X.sup.2)PCl or (R.sup.1X.sup.1)PCl.sub.2, where X.sup.1, X.sup.2, R.sup.1, R.sup.2 are as defined in any of claims

1 to 8, as homogeneous catalyst.

15. A process as claimed in any of claims 6 to 14, wherein the catalyst is removed between step a) and step b).

- . monoolefinic C.sub.5-mononitriles having nonconjugated C.dbd.C and C.dbd.N bonds by hydrocyanation of a 1,3-butadiene-containing hydrocarbon mixture in the presence of a catalyst comprising at least one of the systems as claimed in any of claims 1 to 5.
- . dinitrile by hydrocyanation of a mixture of monoolefinic C.sub.5-mononitriles having nonconjugated C.dbd.C and C.dbd.N bonds in the presence of a catalyst comprising at least one of the systems as claimed in any of claims 1 to 5.
- . adiponitrile by hydrocyanation of a mixture of monoolefinic C.sub.5-mononitriles having nonconjugated C.dbd.C and C.dbd.N bonds in the presence of a catalyst comprising at least one of the systems as claimed in any of claims 1 to 5.

IT 111-69-3P, Adipodinitrile 16529-66-1P, trans-3-Pentenenitrile 16545-78-1P, cis-3-Pentenenitrile 20068-02-4P, cis-2-Methyl-2-butenenitrile 25899-50-7P, cis-2-Pentenenitrile 26294-98-4P, trans-2-Pentenenitrile 28906-50-5P, Methylglutaronitrile 30574-97-1P, trans-2-Methyl-2-butenenitrile
(production of dinitrile monomers from olefinic mononitriles by catalytic isomerization and hydrocyanation)

IT 4635-87-4P, 3-Pentenenitrile
(production of dinitrile monomers from olefinic mononitriles by catalytic isomerization and hydrocyanation)

IT 74-90-8, Hydrocyanic acid, reactions 106-99-0,
1,3-Butadiene, reactions 16529-56-9, 2-Methyl-3-butenenitrile
(production of dinitrile monomers from olefinic mononitriles by catalytic isomerization and hydrocyanation)

TI Catalyst system containing ni(0) for hydrocyanation|

PI US 2004176622 A1 20040909 <--|

AB A catalyst system containing a) Ni (0), b) 4-10 mol per mol Ni (0) according to a) a compound (I) of formula P (X.sup.1R.sup.1) (X.sup.2R.sup.2) (X.sup.3R.sup.3) (I) wherein X.sup.1, X.sup.2, X.sup.3 independently represent oxygen or a single bond R.sup.1, R.sup.2, R.sup.3 represent independently, the same or different organic radicals, and c) 1-4 mol per mol Ni (0) according to a) a compound (II) of formula (II) wherein X.sup.11, X.sup.12, X.sup.13, X.sup.21, X.sup.22, X.sup.23 independently represent oxygen or a single bond, R.sup.11, R.sup.12 independently represent the same or different individual or bridged organic radicals, R.sup.21, R.sup.22 independently represent the same or different, individual or bridged organic radicals, Y represents a bridge group. The invention also relates to a method for the production of mixtures of monoolefin C.sub.5-mononitriles with a n-conjugated C.dbd.C and C.dbd.N bond by hydrocyanation of a hydrocarbon mixture containing 1,3-butadiene in the presence of at least one such system and to a method for the production of a dinitrile by hydrocyanation of a mixture of monoolefin C.sub.5-mononitriles with a non-conjugated C.dbd.C-- and C.dbd.N bond in the presence of at least one such system. ##STR1## [0015] which is suitable as catalyst and to processes for preparing such systems.

SUMM [0016] Systems comprising Ni(0) and a compound (II) which are suitable as catalysts for the hydrocyanation of butadiene to form a mixture of isomeric pentenenitriles and of pentenenitrile to form adiponitrile and processes for preparing them are known per se, for example from U.S.

Pat. No. 3,903,120, U.S. Pat. No. 5,523,453, U.S. Pat. No. 5,981,772, U.S. Pat. No. 6,127,567, U.S. Pat. No. 5,693,843, U.S. Pat. No. 5,847,191, WO 01/14392.

- SUMM [0017] The preparation of these catalyst systems is technically complicated and expensive. This applies particularly since the catalyst systems are gradually decomposed during use and thus have to be discharged and replaced by fresh catalyst.
- SUMM [0018] The direct reaction of metallic nickel as Ni(0) source with compound (II) in the presence or absence of a liquid diluent or hydrogen halide as catalyst leads to a large extent to decomposition of compound (II).
- SUMM [0021] The preparation of the system comprising Ni(0) and compound (II) starting from nickel chloride and zinc as Ni(0) source is known. A disadvantage of this process is the simultaneous formation of the specified catalyst system and zinc chloride.
- SUMM [0022] If the use of the pure catalyst system is envisaged, the zinc chloride firstly has to be removed before use, which is costly.
- SUMM [0023] If the mixture of catalyst system and zinc chloride is used instead of the pure catalyst system, then the work-up of the mixture of exhausted catalyst system and zinc chloride poses a great problem.
- SUMM [0024] A further disadvantage of the catalyst system comprising Ni(0) and compound (II) is that compound (II) can be obtained only by way of a technically complicated and expensive synthesis.
- SUMM [0025] It is an object of the present invention to provide a catalyst system which can be synthesized in a technically simple and economical way and displays selectivities and activities comparable to those of a catalyst system comprising Ni(0) and compound (II), especially in the hydrocyanation of compounds having conjugated olefinic double bonds, e.g. butadiene, and of compounds having one olefinic double bond and another unsaturated group, e.g. 2-pentenenitrile, 3-pentenenitrile, 4-pentenenitrile, 2-pentenoic esters, 3-pentenoic esters or 4-pentenoic esters.
- SUMM [0091] The preparation of the first system in step a) can advantageously be carried out in the presence of a homogeneous or heterogeneous, preferably homogeneous, catalyst.
- SUMM [0092] As homogeneous catalyst, it is advantageous to use a protic acid or a mixture of such protic acids, for example hydrochloric acid.
- SUMM [0093] An advantageous homogeneous catalyst is a compound of the formula
- SUMM [0095] The catalyst used in step a) can be carried over from step a) to step b). It has been found to be advantageous to remove the catalyst from step a) between steps a) and b).
- SUMM [0099] The present invention further provides a process for preparing mixtures of monoolefinic C_nsub.5-mononitriles having nonconjugated C_ndbd.C and C_ndbd.N bonds by hydrocyanation of a 1,3-butadiene-containing hydrocarbon mixture in the presence of a catalyst comprising at least one of the above-described systems according to the present invention.

SUMM [0104] C.sub.4 fractions are, if appropriate, substantially free of alkynes, e.g. propyne or butyne, of 1,2-dienes, e.g. propadiene, and of alkenynes, e.g. vinylacetylene. Otherwise, products in which a C.dbd.C double bond is conjugated with the C.dbd.N bond may be obtained. It is known from "Applied Homogeneous Catalysis with Organometallic Compounds", vol. 1, V. C. H. Weinheim, p. 479, that the conjugated 2-pentenenitrile formed in the isomerization of 2-methyl-3-butenenitrile and 3-pentenenitrile acts as a reaction inhibitor for the second addition of hydrogen cyanide to form adiponitrile. It has been found that the abovementioned conjugated nitriles obtained in the hydrocyanation of an unpretreated C.sub.4 fraction also act as catalyst poisons for the first reaction step of the production of adipic acid, viz. the monoaddition of hydrogen cyanide.

SUMM [0105] For this reason, those components which act as catalyst poisons in catalytic hydrocyanation, in particular alkynes, 1,2-dienes and mixtures thereof, are advantageously removed completely or partially from the hydrocarbon mixture. To remove these components, the C.sub.4 fraction is subjected to a catalytic partial hydrogenation prior to the addition of hydrogen cyanide. This partial hydrogenation is carried out in the presence of a hydrogenation catalyst which is capable of selectively hydrogenating alkynes and 1,2-dienes in the presence of other dienes and monoolefins.

SUMM [0106] Suitable heterogeneous catalyst systems generally comprise a transition metal compound on an inert support. Suitable inorganic supports are the oxides, in particular silicon and aluminum oxides, aluminosilicates, zeolites, carbides, nitrides, etc., customary for this purpose and mixtures thereof. Preferred supports are Al.sub.20.sub.3, SiO.sub.2 and mixtures thereof. In particular, the heterogeneous catalysts used are those described in U.S. Pat. No. 4,587,369; U.S. Pat. No. 4,704,492 and U.S. Pat. No. 4,493,906, which are hereby fully incorporated by reference. Further suitable catalyst systems based on Cu are marketed by Dow Chemical as KLP catalyst.

SUMM [0111] a) charging a reactor with the hydrocarbon mixture, if desired part of the hydrogen cyanide and a hydrocyanation catalyst according to the present invention, if desired one produced in situ, and, if desired, a solvent,

SUMM [0116] The pressure-rated reactor is charged with the partially hydrogenated C.sub.4 fraction, hydrogen cyanide, a hydrocyanation catalyst and, if desired, a solvent prior to commencement of the reaction. Suitable solvents are those mentioned above for the preparation of the catalysts of the present invention, preferably aromatic hydrocarbons such as toluene and xylene or tetrahydrofuran.

SUMM [0120] To complete the conversion, the reaction time can be followed by an after-reaction time of from 0 minutes to about 5 hours, preferably from about 1 hour to 3.5 hours, during which no more hydrogen cyanide is fed into the autoclave. The temperature during this time is kept essentially constant at the level of the reaction temperature previously set. Work-up is carried out by customary methods and comprises separating off the unreacted 1,3-butadiene and the unreacted hydrogen cyanide, e.g. by scrubbing or extraction, and working up the remaining reaction mixture by distillation to separate off the desired product and to recover the still active catalyst.

SUMM [0124] 2. Isomerization of the 2-methyl-3-butenenitrile present in these mixtures to form 3-pentenenitrile and isomerization of the

3-pentenenitrile formed in this way and that already present in the mixture from step 1 to form various n-pentenenitriles. Here, a very high proportion of 3-pentenenitrile or 4-pentenenitrile and a very low proportion of conjugated 2-pentenenitrile and 2-methyl-2-butenenitrile, which may act as catalyst poisons, should be formed.

SUMM [0126] Advantageously, the catalysts of the present invention based on phosphonite ligands are also suitable for the structural isomerization and double bond isomerization in step 2 and/or the second addition of hydrogen cyanide in step 3.

SUMM [0128] Advantageously, the catalysts used according to the present invention not only display a high selectivity to the monoaddition products obtained in the hydrocyanation of 1,3-butadiene-containing hydrocarbon mixtures but they can also be admixed with an excess of hydrogen cyanide in the hydrocyanation without appreciable precipitation of inactive nickel(II) compounds, e.g. nickel(II) cyanide, occurring. In contrast to known hydrocyanation catalysts based on uncomplexed phosphine and phosphite ligands, the catalysts of the formula I are thus suitable not only for continuous hydrocyanation processes in which an excess of hydrogen cyanide in the reaction mixture can generally be effectively avoided but also for semicontinuous processes and batch processes in which a large excess of hydrogen cyanide is generally present. Thus, the catalysts used according to the present invention and the hydrocyanation processes based on them generally allow greater recirculation of catalysts and display longer catalyst operating lives than do known processes. This is advantageous both in terms of improved economics and also from an ecological point of view, since the nickel cyanide formed from the active catalyst by reaction with hydrogen cyanide is highly toxic and has to be worked up or disposed of, which is very costly.

SUMM [0130] A further advantageous embodiment of hydrocyanation and isomerization can be derived from U.S. Pat. No. 6,981,772, whose contents are hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such systems is used in place of the catalysts mentioned in that patent.

SUMM [0131] A further advantageous embodiment of hydrocyanation and isomerization can be derived from U.S. Pat. No. 6,127,567, whose contents are hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such systems is used in place of the catalysts mentioned in that patent.

SUMM [0132] A further advantageous embodiment of a hydrocyanation process can be derived from U.S. Pat. No. 5,693,843, whose contents are hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such systems is used in place of the catalysts mentioned in that patent.

SUMM [0133] A further advantageous embodiment of a hydrocyanation process can be derived from U.S. Pat. No. 5,523,453, whose contents are hereby incorporated by reference, with the proviso that a catalyst system according to the present invention or a mixture of such systems is used in place of the catalysts mentioned in that patent.

DETD [0136] All examples were carried out under a protective argon atmosphere.

DETD [0144] 1 molar equivalent of nickel(0)-(m/p-tolyl phosphite) (0.6 mmol of Ni(0)) was admixed with 365 molar equivalents of 3-pentenenitrile,

the mixture was stirred at 25° C. for 1 hour and heated to 70° C. 1 molar equivalent of ZnCl₂ was added to this mixture and the mixture was stirred for a further 5 minutes. 94 molar equivalents of HCN/hour*Ni in an argon carrier gas stream were passed in. Samples were taken after 30 minutes, 60 minutes and 150 minutes and the following yields (in percent) were determined:

| Time | MGN | ADN | ADN selectivity (%) |
|------|-----|-----|---------------------|
|------|-----|-----|---------------------|

| | | | |
|---------|------|-------|------|
| 30 min | 3.35 | 10.75 | 76.2 |
| 60 min | 6.87 | 26.39 | 79.3 |
| 150 min | 7.11 | 27.82 | 79.6 |

DETD [0148] 1 molar equivalent of Ni(COD)₂ (0.61 mmol of Ni(0)) was admixed with 1 molar equivalent of ligand 1, 4 molar equivalents of m/p-tolyl phosphite (m:p=2:1) and 365 molar equivalents of 3-pentenenitrile, the mixture was stirred at 25° C. for 1 hour and heated to 70° C. 1 molar equivalent of ZnCl₂ was added to this mixture and the mixture was stirred for a further 5 minutes. 133 molar equivalents of HCN/hour*Ni in an argon carrier gas stream were passed in.

DETD [0158] The procedure of Example 10 was repeated (using 0.58 mmol of Ni(0)), except that the catalyst mixture was stirred at 25° C. for 12 hours instead of 1 hour and 122 molar equivalents of HCN/hNi were passed in instead of 43 molar equivalents of HCN/n*Ni.

1. A system comprising a) Ni(0) b) from 4 to 10 mol per mol of Ni(0) in a) of a compound (I) of the formula P(X₁.sup.1R₁.sup.1)(X₂.sup.2R₂.sup.2)(X₃.sup.3R₃.sup.3) (I) where X₁.sup.1, X₂.sup.2, X₃.sup.3 are each oxygen, R₁.sup.1, R₂.sup.2, R₃.sup.3 are, independently of one another, and c) from 1 to 4 mol per mol of Ni(0) in a) of a compound (II) of the formula ##STR5## where X₁₁.sup.11, X₁₂.sup.12, X₁₃.sup.13 X₂₁.sup.21, X₂₂.sup.22, X₂₃.sup.23 are each oxygen, R₁₁.sup.11, R₁₂.sup.12 are identical or different, individual or bridged organic radicals, R₂₁.sup.21, R₂₂.sup.22 are identical or different, individual or bridged organic radicals, Y is a bridging group and R₁.sup.1, R₂.sup.2, R₃.sup.3 are each, independently of one another, a phenyl, o-tolyl, m-tolyl or p-tolyl group, which is suitable as catalyst.

10. A process as claimed in any of claims 6 to 9, wherein the preparation of the first system in step a) is carried out in the presence of a catalyst.

11. A process as claimed in any of claims 6 to 9, wherein the preparation of the first system in step a) is carried out in the presence of a homogeneous catalyst.

12. A process as claimed in any of claims 6 to 9, wherein the preparation of the first system in step a) is carried out in the presence of a protic acid as homogeneous catalyst.

13. A process as claimed in any of claims 6 to 9, wherein the preparation of the first system in step a) is carried out in the presence of hydrogen chloride as homogeneous catalyst.

14. A process as claimed in any of claims 6 to 9, wherein the preparation of the first system in step a) is carried out in the presence of a compound of the formula (R₁.sup.1X₁.sup.1)(R₂.sup.2X₂.sup.2)PCl or (R₁.sup.1X₁.sup.1)PCl₂, where X₁.sup.1, X₂.sup.2, R₁.sup.1, R₂.sup.2

are as defined in any of claims 1 to 8, as homogeneous catalyst.

15. A process as claimed in any of claims 6 to 14, wherein the catalyst is removed between step a) and step b).

19. A process for preparing mixtures of monoolefinic C.sub.5-mononitriles having nonconjugated C.dbd.C and C.dbd.N bonds by hydrocyanation of a 1,3-butadiene-containing hydrocarbon mixture in the presence of a catalyst comprising at least one of the systems as claimed in any of claims 1 to 5.

20. A process for preparing a dinitrile by hydrocyanation of a mixture of monoolefinic C.sub.5-mononitriles having nonconjugated C.dbd.C and C.dbd.N bonds in the presence of a catalyst comprising at least one of the systems as claimed in any of claims 1 to 5.

21. A process for preparing adiponitrile by hydrocyanation of a mixture of monoolefinic C.sub.5-mononitriles having nonconjugated C.dbd.C and C.dbd.N bonds in the presence of a catalyst comprising at least one of the systems as claimed in any of claims 1 to 5.

- IT 111-69-3P, Adipodinitrile 16529-66-1P, trans-3-Pentenenitrile
 16545-78-1P, cis-3-Pentenenitrile 20068-02-4P,
 cis-2-Methyl-2-butenenitrile 25899-50-7P, cis-2-Pentenenitrile
 26294-98-4P, trans-2-Pentenenitrile 28906-50-5P, Methylglutaronitrile
 30574-97-1P, trans-2-Methyl-2-butenenitrile
 (production of dinitrile monomers from olefinic mononitriles by catalytic isomerization and hydrocyanation)
- IT 4635-97-4P, 3-Pentenenitrile
 (production of dinitrile monomers from olefinic mononitriles by catalytic isomerization and hydrocyanation)
- IT 74-90-8, Hydrocyanic acid, reactions 106-99-0,
 1,3-Butadiene, reactions 16529-56-9, 2-Methyl-3-butenenitrile
 (production of dinitrile monomers from olefinic mononitriles by catalytic isomerization and hydrocyanation)
- IT 16529-66-1P, trans-3-Pentenenitrile 16545-78-1P,
 cis-3-Pentenenitrile
 (production of dinitrile monomers from olefinic mononitriles by catalytic isomerization and hydrocyanation)
- RN 16529-66-1 USPATFULL
- CN 3-Pentenenitrile, (3E)- (CA INDEX NAME)

Double bond geometry as shown.



- RN 16545-78-1 USPATFULL
 CN 3-Pentenenitrile, (3Z)- (CA INDEX NAME)

Double bond geometry as shown.



IT 4635-87-4P, 3-Pentenenitrile
 (production of dinitrile monomers from olefinic mononitriles by catalytic
 isomerization and hydrocyanation)
 RN 4635-87-4 USPATFULL
 CN 3-Pentenenitrile (CA INDEX NAME)



IT 74-90-8, Hydrocyanic acid, reactions 106-99-0,
 1,3-Butadiene, reactions
 (production of dinitrile monomers from olefinic mononitriles by catalytic
 isomerization and hydrocyanation)
 RN 74-90-8 USPATFULL
 CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 USPATFULL
 CN 1,3-Butadiene (CA INDEX NAME)



L88 ANSWER 45 OF 60 USPATFULL on STN
 ACCESSION NUMBER: 2004:159447 USPATFULL Full-text
 TITLE: Process of synthesis of compounds having nitrile
 functions from ethylenically unsaturated compounds
 INVENTOR(S): Rosier, Cecile, Soucieu En Jarrest, FRANCE
 Marion, Philippe, Vernaison, FRANCE
 Bourgeois, Damien, Lyon, FRANCE
 PATENT ASSIGNEE(S): RHODIA POLYAMIDE INTERMEDIATES, CEDEX, FRANCE (non-U.S.
 corporation)

| | NUMBER | KIND | DATE |
|---------------------|----------------|------|---------------|
| PATENT INFORMATION: | US 2004122251 | A1 | 20040624 |
| | US 7084293 | B2 | 20060801 |
| APPLICATION INFO.: | US 2003-353912 | A1 | 20030130 (10) |

| | NUMBER | DATE |
|-----------------------|---------------|----------|
| PRIORITY INFORMATION: | FR 2002-16550 | 20021223 |
| DOCUMENT TYPE: | Utility | |
| FILE SEGMENT: | APPLICATION | |

LEGAL REPRESENTATIVE: BURNS, DOANE, SWECKER & MATHIS, L.L.P., P.O. Box 1404,
Alexandria, VA, 22313-1404

NUMBER OF CLAIMS: 27
EXEMPLARY CLAIM: 1
LINE COUNT: 751

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB The present invention relates to a process of hydrocyanation of ethylenically unsaturated organic compounds to compounds having at least one nitrile function, particularly the hydrocyanation of diolefins such as butadiene, or of substituted olefins such as alkene nitrites such as pentenenitriles; the subject hydrocyanation is carried out in the presence of a catalytic system comprising a metallic element and mono- and pluri-dentate organophosphorus ligands.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

SUMM . . . the context of discontinuous performance, there can be charged into a reactor, purged beforehand with an inert gas (such as nitrogen, argon) either a solution containing the whole or a portion of the various constituents, such as the compound to undergo hydrocyanation, .

SUMM [0084] If need be, a slight flushing of the reactor with an inert gas such as nitrogen or argon can be performed in order to expel the hydrogen cyanide which could still be present.

IT 74-90-8, Hydrogen cyanide, reactions 78-79-5, Isoprene, reactions 100-42-5, Styrene, reactions 106-99-0, Butadiene, reactions 110-59-8, Valeronitrile 110-83-8, Cyclohexene, reactions 111-69-3, Adiponitrile 111-78-4, 1,5-Cyclooctadiene 592-42-7, 1,5-Hexadiene 592-51-8, Pentene-4-nitrile 1335-86-0, Methylcyclohexene 4403-61-6, 2-Methyl-2-butenenitrile 4553-62-2, 2-Methyl glutaronitrile 4635-87-4, 3-Pentenenitrile 13284-42-9, 2-Pentenenitrile 16529-56-9, 2-Methyl-3-butenenitrile 17611-82-4, 2-Ethyl succinonitrile 25013-15-4, Methylstyrene 26588-32-9, Vinylnaphthalene (process of synthesis of compds. having nitrile functions from ethylenically unsatd. compds. using organophosphorus ligand-metal complexes)

SUMM [0064] In the context of discontinuous performance, there can be charged into a reactor, purged beforehand with an inert gas (such as nitrogen, argon) either a solution containing the whole or a portion of the various constituents, such as the compound to undergo hydrocyanation, the compounds of formulas (I) and (II), the transition metal compound, the possible reducing agent and solvent; or the said constituents separately. The reactor is generally then brought to the chosen temperature. The hydrogen cyanide is then introduced, preferably in a continuous and regular manner.

SUMM [0084] If need be, a slight flushing of the reactor with an inert gas such as nitrogen or argon can be performed in order to expel the hydrogen cyanide which could still be present.

IT 74-90-8, Hydrogen cyanide, reactions 78-79-5, Isoprene, reactions 100-42-5, Styrene, reactions 106-99-0, Butadiene, reactions 110-59-8, Valeronitrile 110-83-8, Cyclohexene, reactions 111-69-3, Adiponitrile 111-78-4, 1,5-Cyclooctadiene 592-42-7, 1,5-Hexadiene 592-51-8, Pentene-4-nitrile 1335-86-0, Methylcyclohexene 4403-61-6, 2-Methyl-2-butenenitrile 4553-62-2, 2-Methyl glutaronitrile 4635-87-4, 3-Pentenenitrile 13284-42-9, 2-Pentenenitrile 16529-56-9, 2-Methyl-3-butenenitrile 17611-82-4, 2-Ethyl succinonitrile 25013-15-4, Methylstyrene

26588-32-9, Vinylnaphthalene

(process of synthesis of compds. having nitrile functions from ethylenically unsatd. compds. using organophosphorus ligand-metal complexes)

IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,

Butadiene, reactions 4635-87-4, 3-Pentenenitrile

(process of synthesis of compds. having nitrile functions from ethylenically unsatd. compds. using organophosphorus ligand-metal complexes)

RN 74-90-8 USPATFULL

CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 USPATFULL

CN 1,3-Butadiene (CA INDEX NAME)



RN 4635-87-4 USPATFULL

CN 3-Pentenenitrile (CA INDEX NAME)



L88 ANSWER 46 OF 60 USPATFULL on STN

ACCESSION . . .

for hydrocyanation of organic compounds comprising at least a ethylenical bond by reacting hydrogen cyanide, in the presence of a catalytic system comprising a transition metal and an organophosphorus ligand. The organophosphorus ligand is a compound with monophosphanorbornadiene structure. The invention. . .

AB . . . for hydrocyanation of organic compounds comprising at least a ethylenical bond by reacting hydrogen cyanide, in the presence of a catalytic system comprising a transition metal and an organophosphorus ligand. The organophosphorus ligand is a compound with monophosphanorbornadiene structure. The invention. . .

SUMM . . . addition of hydrocyanic acid to organic compounds having at least one ethylenic double bond in the presence of a nickel catalyst and a triaryl phosphite. This reaction can be carried out in the presence or absence of a solvent.

SUMM [0005] The catalyst employed is an organic nickel complex comprising ligands such as phosphines, arsines, stibines, phosphites, arsenites or antimonites.

SUMM [0006] The presence of a promoter for activating the catalyst, such as a boron compound or a metal salt, generally a Lewis acid, is also

recommended in the said patent.

SUMM [0009] This process makes possible correct hydrocyanation, in particular of butadiene and pentenenitriles, and easy separation of the catalytic solution by simple separation by settling and consequently prevents as far as possible discharge of effluents or waste comprising the metals acting as catalyst.

SUMM [0010] However, research is being carried out to find novel catalytic systems which are more effective both as regards catalytic activity and as regards stability.

SUMM . . . the present invention is to provide a novel family of ligands which makes it possible to obtain, with transition metals, catalytic systems exhibiting an improved activity with respect to the known systems.

SUMM . . . hydrocyanation of organic compounds comprising at least one ethylenic bond by reaction with hydrogen cyanide in the presence of a catalytic system comprising a transition metal and an organophosphorus ligand, characterized in that the ligand is a phosphine corresponding to the . . .

SUMM [0065] The catalytic system used for the hydrocyanation according to the process of the invention can be prepared before its introduction into the. . . the appropriate amount of chosen transition metal compound and optionally of reducing agent. It is also possible to prepare the catalytic system "in situ" by simple addition of the phosphine and the transition metal compound to the hydrocyanation reaction medium, before. . .

SUMM . . . batchwise implementation, it is in practice possible to charge to a reactor, purged beforehand using an inert gas (such as nitrogen or argon), either a solution comprising all or a portion of the various constituents, such as the phosphine, the transition metal compound,. . .

SUMM . . . the hydrocyanation of the said nitrile compounds comprising ethylenic unsaturation by reaction with hydrogen cyanide and consists in using a catalytic system in accordance with the present invention with a cocatalyst comprising at least one Lewis acid.

SUMM . . . of linear dinitrile with respect to all the dinitriles formed, and/or to increase the activity and the lifetime of the catalyst.

SUMM [0087] As for the implementation of the basic process of the invention, the catalytic solution used for the hydrocyanation in the presence of Lewis acid can be prepared before its introduction into the reaction. . . transition metal compound, of the Lewis acid and optionally of the reducing agent. It is also possible to prepare the catalytic solution "in situ" by simple mixing of these various constituents.

SUMM . . . the hydrocyanation process of the present invention and in particular by carrying out the hydrocyanation in the presence of the catalyst described above comprising at least one phosphine of formula (I) and at least one transition metal compound, to carry out,. . .

SUMM [0092] In the context of this preferred alternative form, the catalytic system being already present for the reaction for the hydrocyanation of butadiene, it is sufficient to halt any introduction of. . .

SUMM . . . it is possible, if appropriate, to carry out a slight flushing of the reactor using an inert gas, such as nitrogen or argon, for example, in order to drive off the hydrocyanic acid which might still be present.

SUMM [0096] As for the process for the hydrocyanation of compounds comprising ethylenic unsaturation, the catalytic system used for the isomerization can be prepared before its introduction into the reaction region, for example by addition, to. . . appropriate amount of chosen transition metal compound and optionally of the reducing agent. It is also possible to prepare the catalytic system "in situ" by simple

mixing of these various constituents. The amount of transition metal compound and more particularly of . . .

SUMM . . . the preparation of dinitrile compounds by hydrocyanation of an olefin such as butadiene can be carried out by using a catalytic system in accordance with the invention for the stages of formation of the unsaturated nitrites and the stage of isomerization. . . being possible for the reaction for the hydrocyanation of the unsaturated nitrites to dinitriles to be carried out with a catalytic system in accordance with the invention or any other catalytic system already known for this reaction.

SUMM . . . the hydrocyanation of the olefin to unsaturated nitrites and the isomerization of the latter can be carried out with a catalytic system different from that of the invention, the stage of hydrocyanation of the unsaturated nitrites to dinitriles being carried out with a catalytic system in accordance with the invention.

DETD . . . 5.0 eq of PNE or PNA ligand are charged to a reactor equipped with a stirrer and placed under an argon atmosphere. Approximately 1 ml (810 mg, d=0.81, M=81.12 g/mol) of degassed 2M3BN is added. The mixture is stirred and maintained. . .

DETD . . . cosolvent or cosolvents and acetone cyanohydrin (30 eq) are successively introduced at ambient temperature into a Schlenk tube maintained under argon. The mixture is brought with stirring (600 rev/min) to 65° C. for 2 hours and then brought back to ambient.

DETD . . . 56.5 mg (0.21 mmol, M=275 g/mol) of Ni(cod).sub.2 and 50.1 mg (0.21 mmol, M=242 g/mol) of BPh.sub.3 are charged under argon to a 20 ml Schott tube equipped with a septum. The mixture is brought with stirring to 65° C. and. . .

CLM What is claimed is:

. . . hydrocyanation of organic compounds comprising at least one ethylenic bond by reaction with hydrogen cyanide in the presence of a catalytic system comprising a transition metal and an organophosphorus ligand, characterized in that the ligand is a phosphine corresponding to the. . .

. . . ethylenic unsaturation by reaction with hydrogen cyanide, characterized in that the reaction is carried out in the presence of a catalytic system comprising at least one compound of a transition metal, at least one phosphine of formula (I) and a cocatalyst. . .
. . . butadiene is carried out in the absence of hydrogen cyanide, the isomerization being carried out in the presence of a catalyst comprising at least one phosphine of formula (I) and at least one compound of a transition metal.

IT 78-79-5, Isoprene, reactions 106-99-0, Butadiene, reactions 111-78-4, 1,5-Cyclooctadiene 592-42-7, 1,5-Hexadiene (hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)

IT 592-51-8P, 4-Pentenenitrile 4403-61-6P, 2-Methyl-2-butenenitrile 4635-97-4P, 3-Pentenenitrile 16529-56-9P, 2-Methyl-3-butenenitrile

(hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)

IT 74-90-8, Hydrogen cyanide, reactions

(hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles using)

PI US 2004063956 A1 20040401
US 7098358 B2 20060829|

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AB The invention concerns a method for hydrocyanation of ethylenically unsaturated organic compounds into compounds comprising at least a nitrile function. More particularly, it concerns a method for hydrocyanation of

- organic compounds comprising at least a ethylenical bond by reacting hydrogen cyanide, in the presence of a catalytic system comprising a transition metal and an organophosphorus ligand. The organophosphorus ligand is a compound with monophosphanorbornadiene structure. The invention concerns in particular hydrocyanation of butadiene into adiponitrile.]
- SUMM [0003] French Patent No. 1 599 761 discloses a process for the preparation of nitrites by addition of hydrocyanic acid to organic compounds having at least one ethylenic double bond in the presence of a nickel catalyst and a triaryl phosphite. This reaction can be carried out in the presence or absence of a solvent.
- SUMM [0005] The catalyst employed is an organic nickel complex comprising ligands such as phosphines, arsines, stibines, phosphites, arsenites or antimonites.
- SUMM [0006] The presence of a promoter for activating the catalyst, such as a boron compound or a metal salt, generally a Lewis acid, is also recommended in the said patent.
- SUMM [0009] This process makes possible correct hydrocyanation, in particular of butadiene and pentenenitriles, and easy separation of the catalytic solution by simple separation by settling and consequently prevents as far as possible discharge of effluents or waste comprising the metals acting as catalyst.
- SUMM [0010] However, research is being carried out to find novel catalytic systems which are more effective both as regards catalytic activity and as regards stability.
- SUMM [0011] One of the aims of the present invention is to provide a novel family of ligands which makes it possible to obtain, with transition metals, catalytic systems exhibiting an improved activity with respect to the known systems.
- SUMM [0012] To this end, the invention provides a process for the hydrocyanation of organic compounds comprising at least one ethylenic bond by reaction with hydrogen cyanide in the presence of a catalytic system comprising a transition metal and an organophosphorus ligand, characterized in that the ligand is a phosphine corresponding to the following general formula: ##STR1##
- SUMM [0065] The catalytic system used for the hydrocyanation according to the process of the invention can be prepared before its introduction into the reaction region, for example by addition to the phosphine of formula (I), alone or dissolved in a solvent, of the appropriate amount of chosen transition metal compound and optionally of reducing agent. It is also possible to prepare the catalytic system "in situ" by simple addition of the phosphine and the transition metal compound to the hydrocyanation reaction medium, before or after the addition of the compound to be hydrocyanated.
- SUMM [0074] In the context of a batchwise implementation, it is in practice possible to charge to a reactor, purged beforehand using an inert gas (such as nitrogen or argon), either a solution comprising all or a portion of the various constituents, such as the phosphine, the transition metal compound, the possible reducing agent and the possible solvent, or the said constituents separately. Generally, the reactor is then brought to the chosen temperature and then the compound to be hydrocyanated is introduced. The hydrogen cyanide is then itself introduced, preferably continuously and unvaryingly.

- SUMM [0076] An improvement to the process for the hydrocyanation of compounds comprising ethylenic unsaturation according to the present invention relates in particular to the hydrocyanation of the said nitrile compounds comprising ethylenic unsaturation by reaction with hydrogen cyanide and consists in using a catalytic system in accordance with the present invention with a cocatalyst comprising at least one Lewis acid.
- SUMM [0079] The Lewis acid used as cocatalyst makes it possible in particular, in the case of the hydrocyanation of aliphatic nitrites comprising ethylenic unsaturation, to improve the linearity of the dinitriles obtained, that is to say the percentage of linear dinitrile with respect to all the dinitriles formed, and/or to increase the activity and the lifetime of the catalyst.
- SUMM [0087] As for the implementation of the basic process of the invention, the catalytic solution used for the hydrocyanation in the presence of Lewis acid can be prepared before its introduction into the reaction region, for example by addition, to the reaction medium of the phosphine of formula (I), of the appropriate amount of chosen transition metal compound, of the Lewis acid and optionally of the reducing agent. It is also possible to prepare the catalytic solution "in situ" by simple mixing of these various constituents.
- SUMM [0088] It is also possible, under the conditions of the hydrocyanation process of the present invention and in particular by carrying out the hydrocyanation in the presence of the catalyst described above comprising at least one phosphine of formula (I) and at least one transition metal compound, to carry out, in the absence of hydrogen cyanide, isomerization of 2-methyl-3-butenenitrile to pentenenitriles and more generally of branched unsaturated nitrites to linear unsaturated nitrites.
- SUMM [0092] In the context of this preferred alternative form, the catalytic system being already present for the reaction for the hydrocyanation of butadiene, it is sufficient to halt any introduction of hydrogen cyanide to allow the isomerization reaction to take place.
- SUMM [0093] In this alternative form, it is possible, if appropriate, to carry out a slight flushing of the reactor using an inert gas, such as nitrogen or argon, for example, in order to drive off the hydrocyanic acid which might still be present.
- SUMM [0096] As for the process for the hydrocyanation of compounds comprising ethylenic unsaturation, the catalytic system used for the isomerization can be prepared before its introduction into the reaction region, for example by addition, to the reaction medium of the phosphine of formula (I), of the appropriate amount of chosen transition metal compound and optionally of the reducing agent. It is also possible to prepare the catalytic system "in situ" by simple mixing of these various constituents. The amount of transition metal compound and more particularly of nickel compound used and the amount of phosphine of formula (I) are the same as for the hydrocyanation reaction.
- SUMM [0098] However, the preparation of dinitrile compounds by hydrocyanation of an olefin such as butadiene can be carried out by using a catalytic system in accordance with the invention for the stages of formation of the unsaturated nitrites and the stage of isomerization above, it being possible for the reaction for the hydrocyanation of the unsaturated

nitrites to dinitriles to be carried out with a catalytic system in accordance with the invention or any other catalytic system already known for this reaction.

- SUMM [0099] Likewise, the reaction for the hydrocyanation of the olefin to unsaturated nitrites and the isomerization of the latter can be carried out with a catalytic system different from that of the invention, the stage of hydrocyanation of the unsaturated nitrites to dinitriles being carried out with a catalytic system in accordance with the invention.
- DETD [0124] 20 mg (0.073 mmol, M=275 g/mol, 1.0 eq) of Ni(cod).sub.2 and 5.0 eq of PNP or PNA ligand are charged to a reactor equipped with a stirrer and placed under an argon atmosphere. Approximately 1 ml (810 mg, d=0.81, M=81.12 g/mol) of degassed 2M3BN is added. The mixture is stirred and maintained at a temperature of 100°C. in a closed system for 1 hour. The reaction medium is cooled to ambient temperature (approximately 20°C.). The concentrations of the various constituents of the reaction medium are determined by analysis by GC (gas chromatography).
- DETD [0128] The ligand L (5 eq), 3PN (30 eq), Ni(cod).sub.2 (1 eq), ZnCl.sub.2 (1 eq), the degassed cosolvent or cosolvents and acetone cyanohydrin (30 eq) are successively introduced at ambient temperature into a Schlenk tube maintained under argon. The mixture is brought with stirring (600 rev/min) to 65°C. for 2 hours and then brought back to ambient temperature. 3 ml of acetone are introduced to neutralize the remaining HCN. The concentrations of the various components are determined by GC analysis in order to calculate the various degrees of conversion and of selectivity.
- DETD [0131] 0.506 g (6.25 mmol, M=81 g/mol) of 3PN, 340 mg (0.93 mmol, M=366 g/mol) of PNP, 1.96 g of degassed toluene, 56.5 mg (0.21 mmol, M=275 g/mol) of Ni(cod).sub.2 and 50.1 mg (0.21 mmol, M=242 g/mol) of BPPh.sub.3 are charged under argon to a 20 ml Schott tube equipped with a septum. The mixture is brought with stirring to 65°C. and 531 mg (6.24 mmol, M=85 g/mol) of acetone cyanohydrin are injected via the septum and using a syringe driver at a flow rate of 0.19 ml/h. After reacting for 3 h, the mixture is brought back to ambient temperature and neutralized to remove the remaining HCN. The concentrations of the various components are determined by GC analysis in order to calculate the various degrees of conversion and of selectivity.
1. Process for the hydrocyanation of organic compounds comprising at least one ethylenic bond by reaction with hydrogen cyanide in the presence of a catalytic system comprising a transition metal and an organophosphorus ligand, characterized in that the ligand is a phosphine corresponding to the following general formula (I): #STR11## in which: E represents O or S; n represents 0 or 1; R.sub.1, R.sub.4, R.sub.5 and R.sub.6, which are identical or different, represent a hydrogen atom; an optionally substituted, saturated or unsaturated, aliphatic hydrocarbonaceous radical comprising 1 to 40 carbon atoms, the hydrocarbonaceous chain of which is optionally interrupted by a heteroatom; an optionally substituted, monocyclic or polycyclic, saturated, unsaturated or aromatic, carbocyclic or heterocyclic radical; or a saturated or unsaturated, aliphatic hydrocarbonaceous radical, the hydrocarbonaceous chain of which is optionally interrupted by a heteroatom and carries a carbocyclic or heterocyclic radical as defined above, the said radical optionally being substituted; or else R.sub.4 and R.sub.5 form, together with the carbon atoms which carry them, an optionally substituted, saturated or unsaturated, carbocyclic monocycle preferably having from 5 to 7 carbon atoms; R.sub.2 represents a hydrogen atom or the X radical; R.sub.3 represents the X radical or the Y radical; it being understood that one and one alone of the R.sub.2

and R.sub.3 substituents represents the X radical; X being chosen from a monocyclic or bicyclic, aromatic carbocyclic or heterocyclic radical having from 2 to 20 carbon atoms; a 1-alkenyl radical optionally exhibiting one or more additional unsaturations in the hydrocarbonaceous chain and having from 2 to 12 carbon atoms; a 1-alkynyl radical optionally exhibiting one or more additional unsaturations in the hydrocarbonaceous chain and having from 2 to 12 carbon atoms; or a --CN, [(C.sub.1-C.sub.12)alkyl]-carbonyl, [(C.sub.3-C.sub.18)aryl]carbonyl, [(C.sub.1-C.sub.12)alkoxy]-carbonyl, [(C.sub.6-C.sub.18)aryloxy]carbonyl, carbamoyl, [(C.sub.1-C.sub.12)alkyl]carbamoyl or [(di(C.sub.1-C.sub.12)alkyl)carbamoyl radical; and Y taking any one of the meanings of R.sub.1, with the exception of a hydrogen atom; R.sub.7 has the meaning of R.sub.1, R.sub.4, R.sub.5 and R.sub.6 or represents a hydrocarbonaceous radical comprising a carbonyl functional group or a radical of following formulae: ##STR12## in which, A represents a hydrogen atom; (C.sub.1-C.sub.10)alkyl; or (C.sub.6-C.sub.10)aryl or (C.sub.6-C.sub.10)aryl(C.sub.1-C .sub.10)alkyl in which the aryl part is optionally substituted by one or more radicals chosen from (C.sub.1-C.sub.6)alkyl, (C.sub.1-C.sub.6)alkoxy, trifluoromethyl, halogen, di(C.sub.1-C.sub.6)alkylamino, (C.sub.1-C.sub.6)alkoxycarbonyl, carbamoyl, (C.sub.1-C.sub.6)alkylaminocarbonyl and di(C.sub.1-C.sub.6) alkylaminocarbonyl; --Ar.sub.1--Ar.sub.2-- represent: either the divalent radical of formula: ##STR13## in which each of the phenyl nuclei is optionally substituted by one or more Z groups as defined below; or the divalent radical of formula: ##STR14## in which each of the phenyl nuclei is optionally substituted by one or more Z groups as defined below; Z represents (C.sub.1-C.sub.6)alkyl, (C.sub.1-C.sub.6)alkoxy, trifluoromethyl, halogen, (C.sub.1-C.sub.6)alkoxycarbonyl, di(C.sub.1-C.sub.6)alkylamino, (C.sub.1-C.sub.6)alkylaminocarbonyl or di(C.sub.1-C.sub.6)alkylaminocarbonyl; R.sub.8 and R.sub.9, which are identical or different, represent a substituted or unsubstituted aryl radical.

11. Process according to one of the preceding claims for the hydrocyanation to dinitriles of nitrile compounds comprising ethylenic unsaturation by reaction with hydrogen cyanide, characterized in that the reaction is carried out in the presence of a catalytic system comprising at least one compound of a transition metal, at least one phosphine of formula (I) and a cocatalyst comprising at least one Lewis acid.

18. Process according to one of claims 1 to 17, characterized in that the isomerization to pentenenitriles of the 2-methyl-3-butenenitrile present in the reaction mixture originating from the hydrocyanation of butadiene is carried out in the absence of hydrogen cyanide, the isomerization being carried out in the presence of a catalyst comprising at least one phosphine of formula (I) and at least one compound of a transition metal.

IT 78-79-5, Isoprene, reactions 106-99-0, Butadiene, reactions 111-78-4, 1,5-Cyclooctadiene 592-42-7, 1,5-Hexadiene
(hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)

IT 592-51-8P, 4-Pentenenitrile 4403-61-6P, 2-Methyl-2-butenenitrile 4635-87-4F, 3-Pentenenitrile 16529-56-9P, 2-Methyl-3-butenenitrile
(hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)

IT 74-30-8, Hydrogen cyanide, reactions

10/586490

(hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles using)
IT 106-99-0, Butadiene, reactions
(hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)
RN 106-99-0 USPATFULL
CN 1,3-Butadiene (CA INDEX NAME)



IT 4635-87-4F, 3-Pentenenitrile
(hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles)
RN 4635-87-4 USPATFULL
CN 3-Pentenenitrile (CA INDEX NAME)



IT 74-90-8, Hydrogen cyanide, reactions
(hydrocyanation method and catalyst systems for converting ethylenically unsatd. organic compds. into nitriles using)
RN 74-90-8 USPATFULL
CN Hydrocyanic acid (CA INDEX NAME)



L88 ANSWER 47 OF 60 USPATFULL on STN
ACCESSION NUMBER: 2004:70877 USPATFULL Full-text
TITLE: Phosphorus-containing compositions and their use in hydrocyanation, isomerization and hydroformylation reactions
INVENTOR(S): Gagne, Michel R., Carrboro, NC, UNITED STATES
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| | NUMBER | KIND | DATE |
|-----------------------|---|------|---------------|
| PATENT INFORMATION: | US 2004045105 | A1 | 20040318 |
| | US 6924345 | B2 | 20050802 |
| APPLICATION INFO.: | US 2003-659205 | A1 | 20030910 (10) |
| RELATED APPLN. INFO.: | Division of Ser. No. US 2001-994135, filed on 26 Nov 2001, GRANTED, Pat. No. US 6660876 | | |
| DOCUMENT TYPE: | Utility | | |

FILE SEGMENT:

APPLICATION

LEGAL REPRESENTATIVE: E I DU PONT DE NEMOURS AND COMPANY, LEGAL PATENT RECORDS CENTER, BARLEY MILL PLAZA 25/1128, 4417 LANCASTER PIKE, WILMINGTON, DE, 19805

NUMBER OF CLAIMS: 45

EXEMPLARY CLAIM: 1

LINE COUNT: 2484

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB A polymeric, phosphorus-containing composition made by heating, in the presence of an initiator, preferably a free radical initiator, and optionally in the presence of one or more comonomers, at least one substituted phosphonylated 2,2'-dihydroxyl-1,1'-binaphthalene or at least one substituted 2,2'-dihydroxyl-1,1'-biphenylene.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

SUMM . . . unsaturated organic compound can also be substituted with one or more functional groups containing a heteroatom, such as oxygen, sulfur, nitrogen or phosphorus. Examples of these heteroatom-substituted, ethylenically unsaturated, organic compounds include vinyl methyl ether, methyl oleate, oleyl alcohol, 3-pentenenitrile, 4-pentenenitrile, . . .

SUMM . . . into a reactor, such as a tubular reactor, taking care to avoid exposure of oxygen-sensitive catalysts to oxygen from the air. A gaseous mixture of the desired olefinic compound, carbon monoxide and hydrogen, along with any desired diluent, such as nitrogen, helium or argon, is then passed through the reactor while contacting the catalyst. The reaction products are generally liquid at room temperature and. . .

SUMM . . . herein, a non-oxidizing environment is desirable in order to retard oxidative deactivation of the catalyst. Accordingly, an inert atmosphere, e.g., nitrogen, is preferably used, although air can be used, if desired, at the expense of loss of a proportion of the catalyst acitivity through oxidation. Impurities. . .

SUMM . . . in a thermostatically controlled oil bath. HCN was delivered to the flask as an HCN/N₂ gas mixture by bubbling dry nitrogen carrier gas through liquid HCN maintained in an ice bath at 0° C. This provided a vapor stream that was about 35% by volume HCN. The rate of nitrogen gas flow determined the rate of HCN delivery. Samples were periodically analyzed by gas chromatography (GC).

DETD [0161] Aspect 2: Preparation of ethylenically unsaturated, phosphorus-containing bidentate ligand (1): Under nitrogen atmosphere, a 100 mL flask with magnetic stir bar was charged with 2.450 grams of 2,2-bis(4-hydroxy-3-methylphenyl)propane, 0.865 grams of acryloyl. . .

DETD [0206] Aspect 2: Preparation of ethylenically unsaturated ligand (8): Under nitrogen, a 100 mL flask with magnetic stir bar was charged with 1.880 grams of 2,2-bis(4-hydroxy-3-methylphenyl)propane, 0.664 grams of acryloyl chloride. . .

DETD . . . and 5 mL of 3PN in a closed reactor was placed in a 50° C. oil bath and HCN saturated nitrogen was delivered at a nitrogen flow rate of 24 cc/min. The reaction was heated at 50° C. for 1 hour and then at 70° C. for 30 minutes. Nitrogen flow was decreased to 12 cc/min. and the reaction was run at 70° C. for an additional 90 minutes. The. . .

DETD [0230] Aspect 2: Preparation of ethylenically unsaturated ligand (12): Under nitrogen, a 100 mL flask with magnetic stir bar was charged with 0.931 grams of the monoacrylate of 2,2-bis(4-hydroxy-3-methylphenyl)propane (prepared from. . .

DETD . . . to the mixture. The mixture was heated in a 50° C. oil

bath and HCN was delivered with 24 cc/min. nitrogen flow rate. After 90 minutes of reaction, GC analysis indicated 57.6% conversion of 3PN with 92% selectivity to ADN. To . . . but the reaction was allowed to continue at 50° C. for 120 minutes. The mixture was allowed to sit under nitrogen at room temperature overnight. GC analysis indicated 62% conversion of 3PN with 91.3% selectivity to ADN.

DETD . . . begin an additional reaction. The reaction was placed in a 70° C. oil bath and HCN was delivered with a nitrogen flow rate of 30 cc/min. The reaction was then stored at room temperature overnight. The mixture was then heated at 70° C. oil bath with HCN delivered with a nitrogen flow rate of 30 cc/min for 30 minutes. GC analysis indicated 75% conversion of 3PN with selectivity to ADN of. . . was added 5 mL of 3PN. The mixture was heated at 70° C. oil bath with HCN delivered with a nitrogen flow rate of 30 cc/min for 210 minutes. GC analysis indicated 65% conversion of 3PN with selectivity to ADN of. . .

DETD [0246] Aspect 2: Preparation of the diphosphite ligand (13): Under an atmosphere of nitrogen, a cold (-30° C.) Et.sub.20 (5 mL) solution of 6,6'-divinyl-2,2'-dihydroxy-1,1'-binaphthyl (0.051 g, 1.5x10.sup.-4 mol) and Et.sub.3N (0.040, 3.9x10.sup.-4 mol) was. . .

DETD [0248] Aspect 3: Polymerization of the ethylenically unsaturated compound (13) with divinylbenzene: Under an atmosphere of nitrogen, a vial fitted with a Teflon® fluoropolymer resin screwcap was charged with the diphosphite (0.027 g, 2.7x10.sup.-5 mol) described in. . .

DETD [0251] Aspect 2: Preparation of ethylenically unsaturated diphosphite ligand (14): Under an atmosphere of nitrogen, a cold (-30° C.) Et.sub.20 (5 mL) solution of 3,3',4,4',5,5',6,6'-octamethyl-2,2'-dihydroxy-1,1'-biphenyl (0.100 g, 0.67 mmol) and Et.sub.3N (0.152 g, 1.5 mmol). . .

DETD [0252] Aspect 3: Polymerization of the ethylenically unsaturated compound (14) with divinylbenzene and styrene: Under an atmosphere of nitrogen, a vial fitted with a Teflon® fluoropolymer resin screwcap was charged with the diphosphite (0.100 g, 0.09 mmol) described in. . .

DETD [0255] Aspect 5.1: Polymerization of 6,6'-divinyl-2,2'-dihydroxy-1,1'-binaphthyl with styrene: Under nitrogen atmosphere, a vial fitted with a Teflon® fluoropolymer resin screwcap was charged with 6,6'-divinyl-2,2'-dihydroxy-1,1'-binaphthyl (0.500 g, 1.48 mmol), AIBN (0.040). . .

DETD [0256] Aspect 5.2: Formation of the diphosphite ligand from the polymeric precursor of Example 15: Under nitrogen atmosphere, a cold solution (-30° C.) of o-cresol (0.027 g, 0.25 mmol) in toluene (5 mL) was added to a. . .

DETD . . . mL of 3PN. The mixture was heated in a 70 C oil bath and HCN was delivered with 12 cc/min. nitrogen flow rate. After 180 minutes, GC indicated 93.9% conversion to dinitrile with ADN selectivity of 88.4%.

IT 106-99-0, Butadiene, reactions 4635-87-4,
3-Pentenenitrile
(hydrocyanation of; manufacture of unsatd. phosphorus-containing compns.

and
their use in hydrocyanation, isomerization and hydroformylation reactions)

IT 74-85-1, Ethylene, reactions 74-90-8, Hydrogen cyanide,
reactions 79-97-0, 2,2-Bis(4-hydroxy-3-methylphenyl)propane 814-68-6,
Acryloyl chloride 7719-12-2, Phosphorus trichloride 13185-00-7,
6,6'-Dibromo-2,2'-dihydroxy-1,1'-binaphthyl 26567-10-2 31860-10-3

50291-18-4 100930-72-1 532941-08-5 538345-81-2 538346-27-9
 538346-36-0

(manufacture of unsatd. phosphorus-containing compns. and their use in hydrocyanation, isomerization and hydroformylation reactions)

SUMM [0138] The unsaturated organic compound can also be substituted with one or more functional groups containing a heteroatom, such as oxygen, sulfur, nitrogen or phosphorus. Examples of these heteroatom-substituted, ethylenically unsaturated, organic compounds include vinyl methyl ether, methyl oleate, oleyl alcohol, 3-pentenenitrile, 4-pentenenoate, 3-pentenoic acid, 4-pentenoic acid, methyl 3-pentenoate, 7-octen-1-al, acrylonitrile, acrylic acid esters, methyl acrylate, methacrylic acid esters, methyl methacrylate, acrolein, allyl alcohol, 3-pentenal, 4-pentenal, and combinations of two or more thereof.

SUMM [0147] The hydroformylation process can be run in solution or in the gas phase. When the hydroformylation is carried out in the vapor phase, the preferred temperature range is from about 50° C. to about 180° C., most preferably from about 90° C. to 110° C. The temperature must be chosen high enough so as to maintain all of the reactants and products in the vapor phase, but low enough to prevent deterioration of the catalyst. The particular preferred temperature depends to some extent on the catalyst being used, the olefinic compound being used, and the desired reaction rate. The operating pressure is not particularly critical and can be from about 0.1 to 1.0 MPa. The pressure and temperature combination must be chosen so as to maintain reactants and products in the vapor phase. A given catalyst is loaded into a reactor, such as a tubular reactor, taking care to avoid exposure of oxygen-sensitive catalysts to oxygen from the air. A gaseous mixture of the desired olefinic compound, carbon monoxide and hydrogen, along with any desired diluent, such as nitrogen, helium or argon, is then passed through the reactor while contacting the catalyst. The reaction products are generally liquid at room temperature and are conveniently recovered by cooling. The reactor effluent can be directly connected to a sampling valve and can be analyzed by gas chromatography. Aldehydic products, such as linear and branched butyraldehydes obtained from hydroformylation of propylene, can be quantitatively separated and analyzed using a 30M DB-Wax® capillary GC column.

SUMM [0148] For the hydrocyanation, isomerization, and hydroformylation processes described herein, a non-oxidizing environment is desirable in order to retard oxidative deactivation of the catalyst. Accordingly, an inert atmosphere, e.g., nitrogen, is preferably used, although air can be used, if desired, at the expense of loss of a proportion of the catalyst activity through oxidation. Impurities that are detrimental to the catalyst should be kept to a minimum.

SUMM [0159] Hydrocyanation of 3-pentenenitrile was also performed by slowly adding the HCN to the reaction mixture. The catalyst composition and 3-pentenenitrile were heated in a thermostatically controlled oil bath. HCN was delivered to the flask as an HCN/N₂ gas mixture by bubbling dry nitrogen carrier gas through liquid HCN maintained in an ice bath at 0° C. This provided a vapor stream that was about 35% by volume HCN. The rate of nitrogen gas flow determined the rate of HCN delivery. Samples were periodically analyzed by gas chromatography (GC).

DETD [0161] Aspect 2: Preparation of ethylenically unsaturated, phosphorus-containing bidentate ligand (1): Under nitrogen atmosphere, a 100 mL flask with magnetic stir bar was charged with 2.450 grams of 2,2-bis(4-hydroxy-3-methylphenyl)propane, 0.865 grams of acryloyl

chloride, 40 mL of toluene and 8 mL of THF. The mixture was cooled to -30° C. and 1.2 grams of triethylamine in 15 mL of toluene was added. About a quarter of the solvent was removed under vacuum and the mixture cooled to -30° C. To this mixture was added 2.266 grams of the phosphorodichloride of 2-isopropylphenol and 1.2 grams of triethylamine in 10 mL of toluene. The mixture was stirred for one and one-half hours and cooled to -30° C. To the mixture was added 1.157 grams of 3,3',5,5'-tetramethyl-2,2'-biphenol and 1.2 grams of triethylamine. The mixture was kept at -30° C. overnight and then filtered. Solvent was removed to give 5.978 grams of a tacky brown solid (.sup.31P NMR in CDCl₃: 142.21, 142.15, 135.20, 135.11, 134.74, 134.29, 132.01, 131.96, and 131.13).

DETD [0206] Aspect 2: Preparation of ethylenically unsaturated ligand (8): Under nitrogen, a 100 mL flask with magnetic stir bar was charged with 1.880 grams of 2,2-bis(4-hydroxy-3-methylphenyl)propane, 0.664 grams of acryloyl chloride, and 40 mL of THF. The mixture was cooled to -30° C. and a pre-cooled solution (at -30° C.) containing 1 gram of triethylamine in 15 mL of THF was added. The THF was removed under vacuum and the residue dissolved in 50 mL of THF. To this slurry was added 0.503 grams of phosphorus trichloride. The mixture was cooled to -30° C. and a pre-cooled solution containing 0.5 gram of triethylamine in 10 mL of THF was added. After stirring for several days, 0.598 grams of 3,3'-disopropyl-5,5',6,6'-tetramethyl-2,2'-biphenol was added along with 1.2 grams of triethylamine. The mixture was stirred for forty minutes, filtered and the solvent was removed under vacuum to give 3.146 grams of a yellow solid (.sup.31P NMR (CDCl₃): 135.58, 135.25, 135.18, 134.80, 134.71, 132.71, 131.90, 130.80, 127.94, and 127.87).

DETD [0229] Aspect 10: Semibatch 3-pentenenitrile hydrocyanation using nickel catalyst: A reaction mixture of 0.567 grams of the above catalyst, 0.027 grams of zinc chloride, 5 mL of toluene and 5 mL of 3PN in a closed reactor was placed in a 50° C. oil bath and HCN saturated nitrogen was delivered at a nitrogen flow rate of 24 cc/min. The reaction was heated at 50° C. for 1 hour and then at 70° C. for 30 minutes. Nitrogen flow was decreased to 12 cc/min. and the reaction was run at 70° C. for an additional 90 minutes. The temperature was then increased to 80° C. and the reaction was continued for another 90 minutes. GC analysis indicated 68% conversion of 3-pentenenitrile to dinitrile with an ADN selectivity of 89%.

DETD [0230] Aspect 2: Preparation of ethylenically unsaturated ligand (12): Under nitrogen, a 100 mL flask with magnetic stir bar was charged with 0.931 grams of the monoacrylate of 2,2-bis(4-hydroxy-3-methylphenyl)propane (prepared from the reaction of acryloyl chloride with 2,2-bis(4-hydroxy-3-methylphenyl)propane), 0.627 grams of the phosphorodichloride of o-cresol, and 40 mL of toluene. The mixture was cooled to -30° C. and a precooled solution (at -30° C.) containing 0.4 grams of triethylamine in 15 mL of toluene was added. After stirring for 2 hours, .sup.31P NMR in CDCl₃ indicated a peak at 162.8 ppm. The mixture was cooled to -30° C. and 0.448 grams of 3,3',4,4',5,5'-hexamethyl-2,2'-biphenol and 0.65 grams of triethylamine in 2 mL of THF were added. After stirring overnight, the mixture was filtered and the THF removed under vacuum to give a yellow solid. The solid was dissolved in 10 mL of toluene and 0.8 grams of triethylamine was added in 5 mL of THF. The mixture was stirred overnight and filtered. The solvent was removed. .sup.31P NMR indicated some phosphorodichloride still present. The residue was dissolved in THF and 0.75 grams of triethylamine were added. After stirring overnight, the mixture was filtered through silica gel, and the solvent was removed under vacuum. 1.225 Grams of yellow solid were recovered

- (.sup.31P NMR in CDCl₃.sub.3: 137.47, 137.31, 135.29, 135.21, 135.15, 135.00, 134.82, 134.73, 134.40, 134.31, 133.41, 133.40, 132.07, 131.98, 130.44, 127.74, and 127.69).
- DETD [0238] Aspect 10: Hydrocyanation of 3-pentenenitrile: 29 milligrams of ZnCl₂.sub.2 and 5 mL of 3PN were added to the mixture. The mixture was heated in a 50° C. oil bath and HCN was delivered with 24 cc/min. nitrogen flow rate. After 90 minutes of reaction, GC analysis indicated 57.6% conversion of 3PN with 92% selectivity to ADN. To the mixture was added 5 mL of 3PN and the reaction was continued for 90 minutes. At this point, HCN delivery was stopped but the reaction was allowed to continue at 50° C. for 120 minutes. The mixture was allowed to sit under nitrogen at room temperature overnight. GC analysis indicated 62% conversion of 3PN with 91.3% selectivity to ADN.
- DETD [0239] Ligand recycle: At this time, the solvent was removed via syringe from the reactor. 5 mL of toluene, 5 mL of 3PN and 29 milligrams of ZnCl₂.sub.2 were added to begin an additional reaction. The reaction was placed in a 70° C. oil bath and HCN was delivered with a nitrogen flow rate of 30 cc/min. The reaction was then stored at room temperature overnight. The mixture was then heated at 70° C. oil bath with HCN delivered with a nitrogen flow rate of 30 cc/min for 30 minutes. GC analysis indicated 75% conversion of 3PN with selectivity to ADN of 92.2%. To this mixture was added 5 mL of 3PN. The mixture was heated at 70° C. oil bath with HCN delivered with a nitrogen flow rate of 30 cc/min for 210 minutes. GC analysis indicated 65% conversion of 3PN with selectivity to ADN of 91.8%.
- DETD [0246] Aspect 2: Preparation of the diphosphite ligand (13): Under an atmosphere of nitrogen, a cold (-30° C.) Et.sub.2O (5 mL) solution of 6,6'-divinyl-2,2'-dihydroxy-1,1'-binaphthyl (0.051 g, 1.5x10.sup.-4 mol) and Et.sub.3N (0.040, 3.9x10.sup.-4 mol) was slowly added to a Et.sub.2O (5 mL) solution of phosphorochlorodite of 2-isopropoxyphenol (0.140 g, 3.9x10.sup.-4 mol). The solution was allowed to warm up to room temperature and was stirred for one hour. The reaction mixture was filtered through celite and alumina. The volatiles were evaporated to yield a white powder in 67% yield. (0.100 g).
- DETD [0248] Aspect 3: Polymerization of the ethylenically unsaturated compound (13) with divinylbenzene: Under an atmosphere of nitrogen, a vial fitted with a Teflon® fluoropolymer resin screwcap was charged with the diphosphite (0.027 g, 2.7x10.sup.-5 mol) described in example 13, AIBN (0.002 g), DVB (0.1900 g) and THF (0.184 g). This vial was screwed shut and placed in a 70° C. oil bath for 24 hours. After polymerization, the polymer was crushed and the volatiles were removed under vacuum. The resulting white polymer (0.350 g) was insoluble in all organic solvents. Elemental analysis: P found: 1.51%.
- DETD [0251] Aspect 2: Preparation of ethylenically unsaturated diphosphite ligand (14): Under an atmosphere of nitrogen, a cold (-30° C.) Et.sub.2O (5 mL) solution of 3,3',4,4',5,5',6,6'-octamethyl-2,2'-dihydroxy-1,1'-biphenyl (0.100 g, 0.67 mmol) and Et.sub.3N (0.152 g, 1.5 mmol) was slowly added to an Et.sub.2O (5 mL) solution of phosphorochlorodite of trans-2-ethoxy-5-(1-propenyl)phenol (0.631 g, 1.5 mmol). The solution was allowed to warm to room temperature and was stirred for one hour. The reaction mixture was filtered through celite and alumina. The volatiles were evaporated to give 86% yield of a white powder (0.623 g).
- DETD [0252] Aspect 3: Polymerization of the ethylenically unsaturated compound (14) with divinylbenzene and styrene: Under an atmosphere of nitrogen, a vial fitted with a Teflon® fluoropolymer resin screwcap was charged with the diphosphite (0.100 g, 0.09 mmol) described

in example 14, AIBN (0.005 g), DVB (0.40 g), styrene (0.70 g) and THF (1.5 mL). This vial was screwed shut and placed in a 70° C. oil bath for 48 hours, after which DVB (0.75 g) and AIBN (0.005 g) were added and the vial was returned to the oil bath. After 48 hours, the opaque polymer was crushed and the volatiles were removed under vacuum. The resulting white polymer (0.137 g) was insoluble in all organic solvents.

DETD [0255] Aspect 5.1: Polymerization of 6,6'-divinyl-2,2'-dihydroxy-1,1'-binaphthyl with styrene: Under nitrogen atmosphere, a vial fitted with a Teflon® fluoropolymer resin screwcap was charged with 6,6'-divinyl-2,2'-dihydroxy-1,1'-binaphthyl (0.500 g, 1.48 mmol), AIBN (0.040 g), styrene (4.0 mL) and THF (4.0 mL). The vial was screwed shut and placed in a 70° C. oil bath for 24 hours. After polymerization, the polymer was crushed and the volatiles were removed under vacuum. The resulting white polymer (4.8 g) was insoluble in all organic solvents.

DETD [0256] Aspect 5.2: Formation of the diphosphite ligand from the polymeric precursor of Example 15: Under nitrogen atmosphere, a cold solution (-30° C.) of o-cresol (0.027 g, 0.25 mmol) in toluene (5 mL) was added to a solution of the phosphorodichlorodite of phenol (0.045 g, 0.25 mmol) and n-Bu.₃N (0.047 g, 0.25 mmol) in toluene (5 mL). The resulting mixture was allowed to stir at room temperature for 1.5 hours, after which it was cooled to -30° C. This cold solution was added to a cold slurry of polymer from example 15 (0.328 g, 0.10 mmol) and n-Bu.₃N (0.047 g, 0.25 mmol) in toluene (5 mL). This mixture was stirred at room temperature for five hours. The polymer product was isolated by filtration and washed with toluene and acetonitrile. After drying under vacuum, a tacky solid (0.350 g) was obtained.

DETD [0269] Aspect 10: Semi-batch hydrocyanation of 3-pentenenitrile: To 0.388 g of the catalyst from Example 18B was added 19 mg of zinc chloride and 5 mL of 3PN. The mixture was heated in a 70 C oil bath and HCN was delivered with 12 cc/min. nitrogen flow rate. After 180 minutes, GC indicated 93.9% conversion to dinitrile with ADN selectivity of 88.4%.

IT 106-99-0, Butadiene, reactions 4635-87-4,

3-Pentenenitrile

(hydrocyanation of; manufacture of unsatd. phosphorus-containing compns.

and their use in hydrocyanation, isomerization and hydroformylation reactions)

IT 74-85-1, Ethylene, reactions 74-90-8, Hydrogen cyanide, reactions 79-97-0, 2,2-Bis(4-hydroxy-3-methylphenyl)propane 814-68-6, Acryloyl chloride 7719-12-2, Phosphorus trichloride 13185-00-7, 6,6'-dibromo-2,2'-dihydroxy-1,1'-binaphthyl 26567-10-2 31860-10-3 50291-18-4 100930-72-1 532941-08-5 538345-81-2 538346-27-9 538346-36-0

(manufacture of unsatd. phosphorus-containing compns. and their use in hydrocyanation, isomerization and hydroformylation reactions)

IT 106-99-0, Butadiene, reactions 4635-87-4,

3-Pentenenitrile

(hydrocyanation of; manufacture of unsatd. phosphorus-containing compns.

and their use in hydrocyanation, isomerization and hydroformylation reactions)

RN 106-99-0 USPATFULL

CN 1,3-Butadiene (CA INDEX NAME)



RN 4635-87-4 USPATFULL
 CN 3-Pentenenitrile (CA INDEX NAME)



IT 74-90-8, Hydrogen cyanide, reactions
 (manufacture of unsatd. phosphorus-containing compns. and their use in hydrocyanation, isomerization and hydroformylation reactions)
 RN 74-90-8 USPATFULL
 CN Hydrocyanic acid (CA INDEX NAME)



L88 ANSWER 48 OF 60 USPATFULL on STN
 ACCESSION NUMBER: 2003:301062 USPATFULL Full-text
 TITLE: Phosphonite ligands and their use in hydrocyanation
 INVENTOR(S): Lenges, Christian P., Wilmington, DE, UNITED STATES
 Lu, Helen S. M., Wallingford, PA, UNITED STATES
 Ritter, Joachim C., Wilmington, DE, UNITED STATES

| | NUMBER | KIND | DATE | |
|-----------------------|--|------|---------------|-----|
| PATENT INFORMATION: | US 2003212288 | A1 | 20031113 | <-- |
| | US 6846945 | B2 | 20050125 | |
| APPLICATION INFO.: | US 2003-454024 | A1 | 20030604 (10) | |
| RELATED APPLN. INFO.: | Division of Ser. No. US 2002-93655, filed on 7 Mar 2002, PENDING | | | |

| | |
|-----------------------|--|
| DOCUMENT TYPE: | Utility |
| FILE SEGMENT: | APPLICATION |
| LEGAL REPRESENTATIVE: | E I DU PONT DE NEMOURS AND COMPANY, LEGAL PATENT RECORDS CENTER, BARLEY MILL PLAZA 25/1128, 4417 LANCASTER PIKE, WILMINGTON, DE, 19805 |

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|-------------------|-----|
| NUMBER OF CLAIMS: | 10 |
| EXEMPLARY CLAIM: | 1 |
| LINE COUNT: | 411 |

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB Disclosed herein are processes for hydrocyanation and isomerization of olefins by using at least one multidentate phosphonite ligands, including organometallic phosphonite ligands with a Group VIII metal or Group VIII metal compound, and optionally, a Lewis acid promoter.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

SUMM [0002] The present invention concerns the use of catalyst compositions

- comprising a Group VIII metal and a multidentate phosphonite ligand for olefinic hydrocyanation and isomerization processes.
- SUMM [0003] Certain phosphonites have been used as a part of hydrocyanation catalyst systems. U.S. Pat. No. 5,817,850 discloses the use of a catalyst composition in hydroformylation and hydrocyanation reactions. WO9843935 discloses the use of certain phosphonite ligands as part of a catalyst system in a process for producing an aldehyde. WO9946044 relates to a hydroformylation process using phosphonite ligands as part of the catalyst system for hydroformylation reactions. U.S. Pat. No. 6,242,633 discloses a process for the production of nitriles using catalysts containing phosphonite ligands. Further, WO9964155 discloses use of catalysts containing phosphorous ligands in hydrocyanation reactions.
- SUMM [0004] Despite the disclosure of various ligands in hydrocyanation and hydroformylation processes, Catalyst compositions comprising certain multidentate phosphonite ligands show effectiveness and/or higher performance and achieve improvements in rapidity, selectivity, efficiency or stability.
- SUMM [0005] A hydrocyanation process, said process comprising: contacting an ethylenically unsaturated olefin compound with HCN in the presence of a catalyst composition, wherein said catalyst composition comprises a Group VIII metal and a phosphonite ligand wherein the ligand having a structure selected from the group. . . .
- SUMM [0007] The use of a catalyst based on a ligand of structure III for the hydrocyanation and/or the positional isomerization or double bond isomerization of olefins.
- SUMM . . . present invention describes a hydrocyanation process comprising: contacting an ethylenically unsaturated olefin compound with HCN in the presence of a catalyst composition, wherein the catalyst composition comprises a Group VIII metal and a phosphonite ligand having a structure selected from the group consisting of: ##STR2##
- SUMM [0011] The hydrocyanation process described herein may be carried out in the presence of a catalyst precursor composition comprising a Group VIII metal and at least one multidentate phosphonite ligand having a structure III as described. . . .
- SUMM . . . VIII metal or a compound thereof is combined with at least one of the ligand structure III to provide the catalyst. Among the Group VIII metal compounds, nickel, cobalt, and palladium compounds are preferred for hydrocyanation catalysts. A nickel compound is more preferred, and a zero-valent nickel compound having a ligand that can be chemically displaced by. . . .
- SUMM [0013] Zero-valent nickel compounds that can be used for preparing the catalyst of the present invention are disclosed in the art. The preferred zero-valent nickel compounds are Ni(COD).sub.2 (COD is 1,5-cyclooctadiene), Ni(P(O-O-C.sub.6H.sub.4CH.sub.3).sub.3).sub.3. . .
- SUMM . . .
- SUMM [0014] The catalyst of the present invention is prepared by combining the zero-valent nickel compound with at least one molar equivalent of the. . . . of two or more thereof. The unsaturated olefin used in the hydrocyanation process may itself serve as the solvent. The catalyst preparation may be done at room temperature, or at a temperature that is appropriate for the solvent being used, or. . . .
- SUMM . . . at a temperature that is appropriate for the solvent being used, or the hydrocyanation process conditions being used. The resulting catalyst composition may be isolated, if desired.
- SUMM [0018] The catalyst compositions of the present invention may be used with or without a Lewis acid in the hydrocyanation of organic compounds. The hydrocyanation process comprises contacting, in the presence of the catalyst, an olefinic unsaturated organic compound with a hydrogen cyanide-containing fluid under conditions sufficient to produce a

nitrile, wherein the catalyst comprises a Group VIII metal, at least one of the ligands described above, and optionally a Lewis acid as a. . .

SUMM . . . a combination thereof. The hydrocyanation process can be carried out, for example, by charging a suitable vessel with an olefin, catalyst composition, and solvent, if used, to form a reaction mixture. Hydrogen cyanide can be combined initially with other components to. . .

SUMM [0020] Another suitable technique is to charge the vessel with the catalyst and the solvent (if any) to be used, and feed both the unsaturated compound and the HCN slowly to the. . .

SUMM [0021] The molar ratio of ethylenically unsaturated olefin compound to catalyst can be varied from about 10:1 to about 10000:1. The molar ratio of HCN to catalyst generally is varied from about 10:1 to 100,000:1, preferably 100:1 to 5,000:1, for a batch operation. In a continuous operation, such as when using a fixed bed catalyst type of operation, a higher proportion of catalyst can be used such as a molar ratio of about 5:1 to about 100,000:1, and preferably about 100:1 to about 5,000:1, HCN to catalyst.

SUMM . . . The solvent, if used, can be liquid at the reaction temperature and pressure and inert towards the olefin and the catalyst. Suitable solvents include, but are not limited to, hydrocarbons such as benzene, xylene, or combinations thereof; ethers such as tetrahydrofuran. . .

SUMM [0024] The exact temperature is dependent to a certain extent on the particular catalyst being used, the particular olefin being used and the desired reaction rate. Normally, temperatures of from about -25° C. to. . .

SUMM . . . in the presence of one or more Lewis acid promoters to affect both the activity and the selectivity of the catalyst system. The promoter may comprise an inorganic or organometallic compound in which the cation is selected from the group consisting. . . U.S. Pat. No. 4,874,884 (incorporated herein by reference) describes how synergistic combinations of promoters can be chosen to increase the catalytic activity of the catalyst system. Preferred promoters include CdCl₂.sub.2, FeCl₂.sub.2, ZnCl₂.sub.2, B(C₂H₅)₂.sub.3, and (C₂H₅)₂.sub.5Sn(CF₃)₂.sub.3, or (C₂H₅)₂.sub.5BCN. The mole ratio of promoter to Group. . .

SUMM [0038] The catalyst compositions of the present invention may also be used in the isomerization of allylic nitriles. The catalyst composition is combined with the allylic nitrile in a vessel and the isomerization process is carried at from 0 degrees. . .

DETD [0039] The following non-limiting, representative examples illustrate the process and catalyst compositions of this invention. All parts, proportions, and percentages are by weight, unless otherwise indicated. In each example, the following. . .

DETD [0040] Catalyst solutions were prepared by mixing one of the bidentate ligands of the invention and Ni(COD).sub.2 in a molar ratio of 1.1:1 and dissolving this in toluene. To the catalyst solution was added a solution of the promoter in the trans-3PN. The promoter: nickel molar ratio is 1.1:1. The molar. . .

DETD [0045] Catalyst Solution: For a typical multidentate phosphonite ligand 13 mmol of the bidentate ligand and 10 mmol of Ni(COD).sub.2 were combined in toluene to generate 3 g of catalyst solution.

DETD [0047] To a reaction vessel were added 0.1 ml of the catalyst solution. To this was added 0.18 g of the butadiene solution followed by 0.14 g of the HCN solution. The. . .

CLM What is claimed is:

. . . 1. A hydrocyanation process, said process comprising: contacting an ethylenically unsaturated olefin compound with HCN in the presence of a

catalyst composition, wherein said catalyst composition comprises a Group VIII metal and a phosphonite ligand wherein the ligand having a structure selected from the group. . .

10. The use of a catalyst based on a ligand of structure III for the hydrocyanation and/or the positional isomerization or double bond isomerization of olefins.

IT 111-69-3P, Adiponitrile 592-51-8P, 4-Pentenenitrile 1635-87-4P
, 3-Pentenenitrile 16545-78-1P, cis-3-Pentenenitrile

(phosphonite ligands and their use in hydrocyanation)

IT 16529-56-9P, 2-Methyl-3-butenenitrile 16529-66-1P,
trans-3-Pentenenitrile

(phosphonite ligands and their use in hydrocyanation)

IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,

1,3-Butadiene, reactions

(phosphonite ligands and their use in hydrocyanation)

PI US 2003212288 A1 20031113

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US 6846945 B2 20050125|

SUMM [0002] The present invention concerns the use of catalyst compositions comprising a Group VIII metal and a multidentate phosphonite ligand for olefinic hydrocyanation and isomerization processes.

SUMM [0003] Certain phosphonites have been used as a part of hydrocyanation catalyst systems. U.S. Pat. No. 5,817,850 discloses the use of a catalyst composition in hydroformylation and hydrocyanation reactions. WO9843935 discloses the use of certain phosphonite ligands as part of a catalyst system in a process for producing an aldehyde. WO9946044 relates to a hydroformylation process using phosphonite ligands as part of the catalyst system for hydroformylation reactions. U.S. Pat. No. 6,242,633 discloses a process for the production of nitriles using catalysts containing phosphonite ligands. Further, WO9964155 discloses use of catalysts containing phosphorous ligands in hydrocyanation reactions.

SUMM [0004] Despite the disclosure of various ligands in hydrocyanation and hydroformylation processes. Catalyst compositions comprising certain multidentate phosphonite ligands show effectiveness and/or higher performance and achieve improvements in rapidity, selectivity, efficiency or stability.

SUMM [0005] A hydrocyanation process, said process comprising: contacting an ethylenically unsaturated olefin compound with HCN in the presence of a catalyst composition, wherein said catalyst composition comprises a Group VIII metal and a phosphonite ligand wherein the ligand having a structure selected from the group consisting of: ##STR1##

SUMM [0007] The use of a catalyst based on a ligand of structure III for the hydrocyanation and/or the positional isomerization or double bond isomerization of olefins.

SUMM [0008] The present invention describes a hydrocyanation process comprising: contacting an ethylenically unsaturated olefin compound with HCN in the presence of a catalyst composition, wherein the catalyst composition comprises a Group VIII metal and a phosphonite ligand having a structure selected from the group consisting of: ##STR2##

SUMM [0011] The hydrocyanation process described herein may be carried out in the presence of a catalyst precursor composition comprising a Group VIII metal and at least one multidentate phosphonite ligand having a structure III as described above and optionally a Lewis acid.

- SUMM [0012] Generally, a Group VIII metal or a compound thereof is combined with at least one of the ligand structure III to provide the catalyst. Among the Group VIII metal compounds, nickel, cobalt, and palladium compounds are preferred for hydrocyanation catalysts. A nickel compound is more preferred, and a zero-valent nickel compound having a ligand that can be chemically displaced by the ligand structure of the present invention is the most preferred source of Group VIII metal or Group VIII metal compound.
- SUMM [0013] Zero-valent nickel compounds that can be used for preparing the catalyst of the present invention are disclosed in the art. The preferred zero-valent nickel compounds are Ni(COD).sub.2 (COD is 1,5-cyclooctadiene), Ni{P(O-o-C.sub.6H.sub.4CH.sub.3).sub.3}.sub.3 and Ni{P(O-o-C.sub.6H.sub.4CH.sub.3).sub.3}.sub.2(C.sub.6H.sub.4CH.sub.3), all of which are known in the art.
- SUMM [0014] The catalyst of the present invention is prepared by combining the zero-valent nickel compound with at least one molar equivalent of the ligand of structure III of the present invention in a ratio of nickel:bidentate ligand of 1:1. The ligand may be combined with nickel in a solvent, or preferably in the substrate medium. Suitable solvents include, but are not limited to, hydrocarbons such as benzene, xylene, or combinations thereof; ethers such as tetrahydrofuran (THF); nitriles such as acetonitrile, benzonitrile, adiponitrile, or combinations of two or more thereof. The unsaturated olefin used in the hydrocyanation process may itself serve as the solvent. The catalyst preparation may be done at room temperature, or at a temperature that is appropriate for the solvent being used, or the hydrocyanation process conditions.
- SUMM [0016] The divalent nickel compound is combined with the ligand structure III of the present invention in a suitable solvent, preferably the unsaturated olefin, in a ratio of 1:1, or preferably at least 2:1. The combination is then combined with a suitable reducing agent at room temperature, or at a temperature that is appropriate for the solvent being used, or the hydrocyanation process conditions being used. The resulting catalyst composition may be isolated, if desired.
- SUMM [0018] The catalyst compositions of the present invention may be used with or without a Lewis acid in the hydrocyanation of organic compounds. The hydrocyanation process comprises contacting, in the presence of the catalyst, an olefinic unsaturated organic compound with a hydrogen cyanide-containing fluid under conditions sufficient to produce a nitrile, wherein the catalyst comprises a Group VIII metal, at least one of the ligands described above, and optionally a Lewis acid as a promoter. As used herein, the term "fluid" means gas, a liquid, or a combination of these. Any fluid containing about 1 to 100% HCN can be used.
- SUMM [0019] A particularly significant use of the ligands of the present invention is in the hydrocyanation of olefins. In such a process, an olefinic compound such as a diolefinic compound can be converted to a nitrile or a dinitrile, or a combination thereof. The hydrocyanation process can be carried out, for example, by charging a suitable vessel with an olefin, catalyst composition, and solvent, if used, to form a reaction mixture. Hydrogen cyanide can be combined initially with other components to form the mixture. However, it is preferred that HCN be added slowly to the mixture after other components have been combined. Hydrogen cyanide can be delivered as a liquid or as a vapor to the vessel. As an alternative, a cyanohydrin can be used as the source of

HCN. See, for example, U.S. Pat. No. 3,655,723, incorporated herein by reference.

- SUMM [0020] Another suitable technique is to charge the vessel with the catalyst and the solvent (if any) to be used, and feed both the unsaturated compound and the HCN slowly to the reaction mixture.
- SUMM [0021] The molar ratio of ethylenically unsaturated olefin compound to catalyst can be varied from about 10:1 to about 10000:1. The molar ratio of HCN to catalyst generally is varied from about 10:1 to 100,000:1, preferably 100:1 to 5,000:1, for a batch operation. In a continuous operation, such as when using a fixed bed catalyst type of operation, a higher proportion of catalyst can be used such as a molar ratio of about 5:1 to about 100,000:1, and preferably about 100:1 to about 5,000:1, HCN to catalyst.
- SUMM [0023] The hydrocyanation can be carried out with or without a solvent. The solvent, if used, can be liquid at the reaction temperature and pressure and inert towards the olefin and the catalyst. Suitable solvents include, but are not limited to, hydrocarbons such as benzene, xylene, or combinations thereof; ethers such as tetrahydrofuran (THF); nitrites such as acetonitrile, benzonitrile, adiponitrile, or combinations of two or more thereof. The unsaturated olefin to be hydrocyanated can itself serve as the solvent. Hydrocyanation can also be carried out in the gas phase.
- SUMM [0024] The exact temperature is dependent to a certain extent on the particular catalyst being used, the particular olefin being used and the desired reaction rate. Normally, temperatures of from about -25° C. to about 200° C. can be used with the range of 0° C. to 150° C. being preferred.
- SUMM [0031] The process of this invention can be carried out in the presence of one or more Lewis acid promoters to affect both the activity and the selectivity of the catalyst system. The promoter may comprise an inorganic or organometallic compound in which the cation is selected from the group consisting of scandium, titanium, vanadium, chromium, manganese, iron, cobalt, copper, zinc, boron, aluminum, yttrium, zirconium, niobium, molybdenum, cadmium, rhenium and tin. Examples include, but are not limited to, ZnBr₂, ZnI₂, ZnCl₂, ZnSO₄, CuCl₂, CuCl, Cu(O₂SCF₂)₂, CoCl₂, Col₂, FeI₂, FeCl₂, FeCl₂²(THF)₂, TiCl₂, TiCl₂⁴(THF)₂, MnCl₂, ScCl₃, AlCl₃, (C₂H₅CH₂)AlCl₂, (C₂H₅CH₂)₂AlCl, (iso-C₄H₉)₂AlCl, Ph₂AlCl, PhAlCl₂, ReCl₅, ZrCl₄, NbCl₅, VCl₃, CrCl₂, MoCl₅, YCl₃, CdCl₂, LaCl₃, Er(O₂SCF₂)₃, Yb(O₂CCF₃)₃, SmCl₃, B(C₂H₅CH₂)₂, TaCl₅. Suitable promoters known in the art. These include metal salts, such as ZnCl₂, Col₂, and SnCl₂, and organometallic compounds (such as R₂AlCl₂, R₂SnO₂SCF₂, and R₂SnCl₄, where R₂ is an alkyl or aryl group). U.S. Pat. No. 4,874,884 (incorporated herein by reference) describes how synergistic combinations of promoters can be chosen to increase the catalytic activity of the catalyst system. Preferred promoters include CdCl₂, FeCl₂, ZnCl₂, B(C₂H₅CH₂)₂, and (C₂H₅CH₂)₂Sn(CF₃)₂, CH₂CO₂CH₂Sn(CF₃)₂, or (C₂H₅CH₂)₂BCN. The mole ratio of promoter to Group VIII metal present in the reaction can be within the range of about 1:16 to about 50:1.

SUMM [0038] The catalyst compositions of the present invention may also be used in the isomerization of allylic nitrites. The catalyst composition is combined with the allylic nitrile in a vessel and the isomerization process is carried at from 0 degrees C. to 150 degrees C., and preferably from 80 degrees C. to 120 degrees C. A solvent may be used. Examples of a suitable solvent include but are not limited to, hydrocarbons such as benzene, xylene, or combinations thereof; ethers such as tetrahydrofuran (THF); nitriles such as acetonitrile, benzonitrile, adiponitrile, or combinations of two or more thereof.

DETD [0039] The following non-limiting, representative examples illustrate the process and catalyst compositions of this invention. All parts, proportions, and percentages are by weight, unless otherwise indicated. In each example, the following procedure was used unless otherwise noted.

DETD [0040] Catalyst solutions were prepared by mixing one of the bidentate ligands of the invention and Ni(COD).sub.2 in a molar ratio of 1.1:1 and dissolving this in toluene. To the catalyst solution was added a solution of the promoter in the trans-3PN. The promoter: nickel molar ratio is 1.1:1. The molar ratio of trans-3PN to Ni was 200 equivalents. The reaction vessel was heated to the temperature as described in the following Tables and hydrogen cyanide was delivered by slow evaporation of the hydrogen cyanide from a reservoir connected to the reaction vessel by a feed tube in an otherwise closed reaction system. The reaction was analyzed after 15 hours. The reaction mixture was analyzed using standard Gas Chromatograph methodology. Tables I-through III list the conversion of pentenenitriles to dinitriles and the selectivity to adiponitrile, defined as the ratio of adiponitrile over all dinitriles, in this hydrocyanation reaction.

TABLE I

| Promoter: ZnCl ₂ .sub.2 | | |
|------------------------------------|-------------|------|
| Conversion | Selectivity | |
| ligand | | to |
| Dinitrile to ADN | | |
| <i>50° C.</i> | | |
| Example 1 | ##STR6## | 73.8 |
| 91.0 | | |
| Example 2 | ##STR7## | 2.2 |
| 81.8 | | |
| Example 3 | ##STR8## | 57.4 |
| 90.6 | | |
| Example 4 | ##STR9## | 32.7 |
| 87.6 | | |
| Example 5 | ##STR10## | 87.5 |
| 88.7 | | |
| Example 6 | ##STR11## | 28.2 |
| 85.1 | | |
| <i>80° C.</i> | | |
| Example 7 | ##STR12## | 13.5 |
| 82.9 | | |

Example 8 ##STR13## 58.8
 73.0

Example 9 ##STR14## 66.0
 77.2

Example 10 ##STR15## 83.2
 73.7

DETD [0045] Catalyst Solution: For a typical multidentate phosphonite ligand 13 mmol of the bidentate ligand and 10 mmol of Ni(COD).sub.2 were combined in toluene to generate 3 g of catalyst solution.

DETD [0047] To a reaction vessel were added 0.1 ml of the catalyst solution. To this was added 0.18 g of the butadiene solution followed by 0.14 g of the HCN solution. The vessel was sealed and placed in a reactor set at 100° C. Samples were removed after three hours.

1. A hydrocyanation process, said process comprising: contacting an ethylenically unsaturated olefin compound with HCN in the presence of a catalyst composition, wherein said catalyst composition comprises a Group VIII metal and a phosphonite ligand wherein the ligand having a structure selected from the group consisting of: ##STR28## wherein X and Q are as described in Formula II, and L is a linking group selected from the group consisting of -CR1 R2--, --O--, --S--, --CO-- (wherein each of R1-R2 are independent of one another, are a hydrogen atom, a C1-12 alkyl group, or an aryl group), and each of m and m' which are independent of each other, are 0 or 1.

10. The use of a catalyst based on a ligand of structure III for the hydrocyanation and/or the positional isomerization or double bond isomerization of olefins.

IT 111-69-3P, Adiponitrile 592-51-8P, 4-Pentenenitrile 4635-87-4P
 , 3-Pentenenitrile 16545-78-1P, cis-3-Pentenenitrile
 (phosphonite ligands and their use in hydrocyanation)

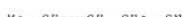
IT 16529-56-9P, 2-Methyl-3-butenenitrile 16529-66-1P,
 trans-3-Pentenenitrile
 (phosphonite ligands and their use in hydrocyanation)

IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,
 1,3-Butadiene, reactions
 (phosphonite ligands and their use in hydrocyanation)

IT 4635-87-4P, 3-Pentenenitrile 16545-78-1P,
 cis-3-Pentenenitrile
 (phosphonite ligands and their use in hydrocyanation)

RN 4635-87-4 USPATFULL

CN 3-Pentenenitrile (CA INDEX NAME)



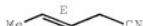
RN 16545-78-1 USPATFULL
 CN 3-Pentenenitrile, (3Z)- (CA INDEX NAME)

Double bond geometry as shown.



IT 16529-66-1E, trans-3-Pentenenitrile
 (phosphonite ligands and their use in hydrocyanation)
 RN 16529-66-1 USPATFULL
 CN 3-Pentenenitrile, (3E)- (CA INDEX NAME)

Double bond geometry as shown.



IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,
 1,3-Butadiene, reactions
 (phosphonite ligands and their use in hydrocyanation)
 RN 74-90-8 USPATFULL
 CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 USPATFULL
 CN 1,3-Butadiene (CA INDEX NAME)



L88 ANSWER 49 OF 60 USPATFULL on STN
 ACCESSION NUMBER: 2003:277345 USPATFULL Full-text
 TITLE: Phosphonite ligands and their use in hydrocyanation
 INVENTOR(S): Lenges, Christian P., Wilmington, DE, UNITED STATES
 Lu, Helen S. M., Wallingford, PA, UNITED STATES
 Ritter, Joachim C., Wilmington, DE, UNITED STATES

| | NUMBER | KIND | DATE | |
|-----------------------|--|------|---------------|-----|
| PATENT INFORMATION: | US 2003195372 | A1 | 20031016 | <-- |
| | US 6737539 | B2 | 20040518 | |
| APPLICATION INFO.: | US 2003-454074 | A1 | 20030604 (10) | |
| RELATED APPLN. INFO.: | Division of Ser. No. US 2002-93655, filed on 7 Mar 2002, PENDING | | | |
| DOCUMENT TYPE: | Utility | | | |
| FILE SEGMENT: | APPLICATION | | | |
| LEGAL REPRESENTATIVE: | E I DU PONT DE NEMOURS AND COMPANY, LEGAL PATENT | | | |

RECORDS CENTER, BARLEY MILL PLAZA 25/1128, 4417
LANCASTER PIKE, WILMINGTON, DE, 19805

NUMBER OF CLAIMS: 10
EXEMPLARY CLAIM: 1
LINE COUNT: 415

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB Disclosed herein are processes for hydrocyanation and isomerization of olefins by using at least one multidentate phosphonite ligands, including organometallic phosphonite ligands with a Group VIII metal or Group VIII metal compound, and optionally, a Lewis acid promoter.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

SUMM [0002] The present invention concerns the use of catalyst compositions comprising a Group VIII metal and a multidentate phosphonite ligand for olefinic hydrocyanation and isomerization processes.

SUMM [0003] Certain phosphonites have been used as a part of hydrocyanation catalyst systems. U.S. Pat. No. 5,817,850 discloses the use of a catalyst composition in hydroformylation and hydrocyanation reactions. WO9843935 discloses the use of certain phosphonite ligands as part of a catalyst system in a process for producing an aldehyde. WO9946044 relates to a hydroformylation process using phosphonite ligands as part of the catalyst system for hydroformylation reactions. U.S. Pat. No. 6,242,633 discloses a process for the production of nitriles using catalysts containing phosphonite ligands. Further, WO9964155 discloses use of catalysts containing phosphorous ligands in hydrocyanation reactions.

SUMM [0004] Despite the disclosure of various ligands in hydrocyanation and hydroformylation processes. Catalyst compositions comprising certain multidentate phosphonite ligands show effectiveness and/or higher performance and achieve improvements in rapidity, selectivity, efficiency or stability.

SUMM [0005] A hydrocyanation process, said process comprising: contacting an ethylenically unsaturated olefin compound with HCN in the presence of a catalyst composition, wherein said catalyst composition comprises a Group VIII metal and a phosphonite ligand wherein the ligand having a structure selected from the group. . .

SUMM [0007] The use of a catalyst based on a ligand of structure II for the hydrocyanation and/or the positional isomerization or double bond isomerization of olefins.

SUMM . . . present invention describes a hydrocyanation process comprising: contacting an ethylenically unsaturated olefin compound with HCN in the presence of a catalyst composition, wherein the catalyst composition comprises a Group VIII metal and a phosphonite ligand having a structure selected from the group consisting of: ##STR2##
[0011] The hydrocyanation process described herein may be carried out in the presence of a catalyst precursor composition comprising a Group VIII metal and at least one multidentate phosphonite ligand having a structure II I as. . .

SUMM . . . VII metal or a compound thereof is combined with at least one of the ligand structure II to provide the catalyst. Among the Group VII metal compounds, nickel, cobalt, and palladium compounds are preferred for hydrocyanation catalysts. A nickel compound is more preferred, and a zero-valent nickel compound having a ligand that can be chemically displaced by. . .

SUMM [0013] Zero-valent nickel compounds that can be used for preparing the catalyst of the present invention are disclosed in the art. The preferred zero-valent nickel compounds are Ni(COD).sub.2 (COD is 1,5-cyclooctadiene), Ni(P(O-o-C.sub.6H.sub.4CH.sub.3).sub.3).sub.3. . .

SUMM [0014] The catalyst of the present invention is prepared by combining the zero-valent nickel compound with at least one molar equivalent of the . . . of two or more thereof. The unsaturated olefin used in the hydrocyanation process may itself serve as the solvent. The catalyst preparation may be done at room temperature, or at a temperature that is appropriate for the solvent being used, or. . .

SUMM . . . at a temperature that is appropriate for the solvent being used, or the hydrocyanation process conditions being used. The resulting catalyst composition may be isolated, if desired.

SUMM [0018] The catalyst compositions of the present invention may be used with or without a Lewis acid in the hydrocyanation of organic compounds. The hydrocyanation process comprises contacting, in the presence of the catalyst, an olefinic unsaturated organic compound with a hydrogen cyanide-containing fluid under conditions sufficient to produce a nitrile, wherein the catalyst comprises a Group VIII metal, at least one of the ligands described above, and optionally a Lewis acid as a . . .

SUMM . . . a combination thereof. The hydrocyanation process can be carried out, for example, by charging a suitable vessel with an olefin, catalyst composition, and solvent, if used, to form a reaction mixture. Hydrogen cyanide can be combined initially with other components to. . .

SUMM [0020] Another suitable technique is to charge the vessel with the catalyst and the solvent (if any) to be used, and feed both the unsaturated compound and the HCN slowly to the. . .

SUMM [0021] The molar ratio of ethylenically unsaturated olefin compound to catalyst can be varied from about 10:1 to about 10000:1. The molar ratio of HCN to catalyst generally is varied from about 10:1 to 100,000:1, preferably 100:1 to 5,000:1, for a batch operation. In a continuous operation, such as when using a fixed bed catalyst type of operation, a higher proportion of catalyst can be used such as a molar ratio of about 5:1 to about 100,000:1, and preferably about 100:1 to about 5,000:1, HCN to catalyst.

SUMM . . . The solvent, if used, can be liquid at the reaction temperature and pressure and inert towards the olefin and the catalyst. Suitable solvents include, but are not limited to, hydrocarbons such as benzene, xylene, or combinations thereof; ethers such as tetrahydrofuran. . .

SUMM [0024] The exact temperature is dependent to a certain extent on the particular catalyst being used, the particular olefin being used and the desired reaction rate. Normally, temperatures of from about -25° C. to. . .

SUMM . . . in the presence of one or more Lewis acid promoters to affect both the activity and the selectivity of the catalyst system. The promoter may comprise an inorganic or organometallic compound in which the cation is selected from the group consisting. . . U.S. Pat. No. 4,874,884 (incorporated herein by reference) describes how synergistic combinations of promoters can be chosen to increase the catalytic activity of the catalyst system. Preferred promoters include CdCl₂.sub.2, FeCl₂.sub.2, ZnCl₂.sub.2, B(C₂H₅)₂.sub.3, and (C₂H₅)₂Sn(CF₃)₂.sub.3, CH₂=CH-C₂H₅.sub.2, or (C₂H₅)₂Sn(CF₃)₂.sub.3BCN. The mole ratio of promoter to Group. . .

SUMM [0038] The catalyst compositions of the present invention may also be used in the isomerization of allylic nitrites. The catalyst composition is combined with the allylic nitrile in a vessel and the isomerization process is carried out from 0 degrees. . .

DETD [0039] The following non-limiting, representative examples illustrate the process and catalyst compositions of this invention. All parts, proportions, and percentages are by weight, unless otherwise indicated. In each example, the following. . .

- DETD [0040] Catalyst solutions were prepared by mixing one of the bidentate ligands of the invention and Ni(COD).sub.2 in a molar ratio of 1.1:1 and dissolving this in toluene. To the catalyst solution was added a solution of the promoter in the trans-3PN. The promoter: nickel molar ratio is 1.1:1. The molar. . .
- DETD [0045] Catalyst Solution: For a typical multidente phosphonite ligand 13 mmol of the bidentate ligand and 10 mmol of Ni(COD).sub.2 were combined in toluene to generate 3 g of catalyst solution.
- DETD [0047] To a reaction vessel were added 0.1 ml of the catalyst solution. To this was added 0.18 g of the butadiene solution followed by 0.14 g of the HCN solution. The. . .
- CLM What is claimed is:
- . . 1. A hydrocyanation process, said process comprising: contacting an ethylenically unsaturated olefin compound with HCN in the presence of a catalyst composition, wherein said catalyst composition comprises a Group VIII metal and a phosphonite ligand wherein the ligand having a structure selected from the group. . .
 - 10. The use of a catalyst based on a ligand of structure II for the hydrocyanation and/or the positional isomerization or double bond isomerization of olefins.
 - . .
- IT 111-69-3P, Adiponitrile 592-51-8P, 4-Pentenenitrile 4635-87-4P
, 3-Pentenenitrile 16545-78-1P, cis-3-Pentenenitrile
(phosphonite ligands and their use in hydrocyanation)
- IT 16529-56-9P, 2-Methyl-3-butenenitrile 16529-66-1P,
trans-3-Pentenenitrile
(phosphonite ligands and their use in hydrocyanation)
- IT 74-90-9, Hydrogen cyanide, reactions 106-99-0,
1,3-Butadiene, reactions
(phosphonite ligands and their use in hydrocyanation)
- PI US 2003195372 A1 20031016
US 6737539 B2 20040518| <--|
- SUMM [0002] The present invention concerns the use of catalyst compositions comprising a Group VIII metal and a multidente phosphonite ligand for olefinic hydrocyanation and isomerization processes.
- SUMM [0003] Certain phosphonites have been used as a part of hydrocyanation catalyst systems. U.S. Pat. No. 5,817,850 discloses the use of a catalyst composition in hydroformylation and hydrocyanation reactions. WO9843935 discloses the use of certain phosphonite ligands as part of a catalyst system in a process for producing an aldehyde. WO9946044 relates to a hydroformylation process using phosphonite ligands as part of the catalyst system for hydroformylation reactions. U.S. Pat. No. 6,242,633 discloses a process for the production of nitriles using catalysts containing phosphonite ligands. Further, WO9964155 discloses use of catalysts containing phosphorous ligands in hydrocyanation reactions.
- SUMM [0004] Despite the disclosure of various ligands in hydrocyanation and hydroformylation processes. Catalyst compositions comprising certain multidente phosphonite ligands show effectiveness and/or higher performance and achieve improvements in rapidity, selectivity, efficiency or stability.
- SUMM [0005] A hydrocyanation process, said process comprising: contacting an ethylenically unsaturated olefin compound with HCN in the presence of a catalyst composition, wherein said catalyst composition comprises a Group VIII metal and a phosphonite ligand wherein the ligand having a structure selected from the group consisting of: ##STR1##

- SUMM [0007] The use of a catalyst based on a ligand of structure II for the hydrocyanation and/or the positional isomerization or double bond isomerization of olefins.
- SUMM [0008] The present invention describes a hydrocyanation process comprising: contacting an ethylenically unsaturated olefin compound with HCN in the presence of a catalyst composition, wherein the catalyst composition comprises a Group VIII metal and a phosphonite ligand having a structure selected from the group consisting of: ##STR2##
- SUMM [0011] The hydrocyanation process described herein may be carried out in the presence of a catalyst precursor composition comprising a Group VIII metal and at least one multidentate phosphonite ligand having a structure II I as described above and optionally a Lewis acid.
- SUMM [0012] Generally, a Group VII metal or a compound thereof is combined with at least one of the ligand structure II to provide the catalyst. Among the Group VII metal compounds, nickel, cobalt, and palladium compounds are preferred for hydrocyanation catalysts. A nickel compound is more preferred, and a zero-valent nickel compound having a ligand that can be chemically displaced by the ligand structure of the present invention is the most preferred source of Group VIII metal or Group VIII metal compound.
- SUMM [0013] Zero-valent nickel compounds that can be used for preparing the catalyst of the present invention are disclosed in the art. The preferred zero-valent nickel compounds are Ni(COD).sub.2 (COD is 1,5-cyclooctadiene), Ni{P(O-o-C.sub.6H.sub.4CH.sub.3).sub.3}.sub.3 and Ni{P(O-o-C.sub.6H.sub.4CH.sub.3).sub.3}.sub.2(C.sub.6H.sub.4CH.sub.3), all of which are known in the art.
- SUMM [0014] The catalyst of the present invention is prepared by combining the zero-valent nickel compound with at least one molar equivalent of the ligand of structure II of the present invention in a ratio of nickel:bidentate ligand of 1:1. The ligand may be combined with nickel in a solvent, or preferably in the substrate medium. Suitable solvents include, but are not limited to, hydrocarbons such as benzene, xylene, or combinations thereof; ethers such as tetrahydrofuran (THF); nitriles such as acetonitrile, benzonitrile, adiponitrile, or combinations of two or more thereof. The unsaturated olefin used in the hydrocyanation process may itself serve as the solvent. The catalyst preparation may be done at room temperature, or at a temperature that is appropriate for the solvent being used, or the hydrocyanation process conditions.
- SUMM [0016] The divalent nickel compound is combined with the ligand structure II of the present invention in a suitable solvent, preferably the unsaturated olefin, in a ratio of 1:1, or preferably at least 2:1. The combination is then combined with a suitable reducing agent at room temperature, or at a temperature that is appropriate for the solvent being used, or the hydrocyanation process conditions being used. The resulting catalyst composition may be isolated, if desired.
- SUMM [0018] The catalyst compositions of the present invention may be used with or without a Lewis acid in the hydrocyanation of organic compounds. The hydrocyanation process comprises contacting, in the presence of the catalyst, an olefinic unsaturated organic compound with a hydrogen cyanide-containing fluid under conditions sufficient to produce a nitrile, wherein the catalyst comprises a Group VIII metal, at least one of the ligands described above, and optionally a Lewis acid as a promoter. As used herein, the term "fluid" means gas, a liquid, or a

combination of these. Any fluid containing about 1 to 100% HCN can be used.

SUMM [0019] A particularly significant use of the ligands of the present invention is in the hydrocyanation of olefins. In such a process, an olefinic compound such as a diolefinic compound can be converted to a nitrile or a dinitrile, or a combination thereof. The hydrocyanation process can be carried out, for example, by charging a suitable vessel with an olefin, catalyst composition, and solvent, if used, to form a reaction mixture. Hydrogen cyanide can be combined initially with other components to form the mixture. However, it is preferred that HCN be added slowly to the mixture after other components have been combined. Hydrogen cyanide can be delivered as a liquid or as a vapor to the vessel. As an alternative, a cyanohydrin can be used as the source of HCN. See, for example, U.S. Pat. No. 3,655,723, incorporated herein by reference.

SUMM [0020] Another suitable technique is to charge the vessel with the catalyst and the solvent (if any) to be used, and feed both the unsaturated compound and the HCN slowly to the reaction mixture.

SUMM [0021] The molar ratio of ethylenically unsaturated olefin compound to catalyst can be varied from about 10:1 to about 10000:1. The molar ratio of HCN to catalyst generally is varied from about 10:1 to 100,000:1, preferably 100:1 to 5,000:1, for a batch operation. In a continuous operation, such as when using a fixed bed catalyst type of operation, a higher proportion of catalyst can be used such as a molar ratio of about 5:1 to about 100,000:1, and preferably about 100:1 to about 5,000:1, HCN to catalyst.

SUMM [0023] The hydrocyanation can be carried out with or without a solvent. The solvent, if used, can be liquid at the reaction temperature and pressure and inert towards the olefin and the catalyst. Suitable solvents include, but are not limited to, hydrocarbons such as benzene, xylene, or combinations thereof; ethers such as tetrahydrofuran (THF); nitriles such as acetonitrile, benzonitrile, adiponitrile, or combinations of two or more thereof. The unsaturated olefin to be hydrocyanated can itself serve as the solvent. Hydrocyanation can also be carried out in the gas phase.

SUMM [0024] The exact temperature is dependent to a certain extent on the particular catalyst being used, the particular olefin being used and the desired reaction rate. Normally, temperatures of from about -25° C. to about 200° C. can be used with the range of 0° C. to 150° C. being preferred.

SUMM [0031] The process of this invention can be carried out in the presence of one or more Lewis acid promoters to affect both the activity and the selectivity of the catalyst system. The promoter may comprise an inorganic or organometallic compound in which the cation is selected from the group consisting of scandium, titanium, vanadium, chromium, manganese, iron, cobalt, copper, zinc, boron, aluminum, yttrium, zirconium, niobium, molybdenum, cadmium, rhenium and tin. Examples include, but are not limited to, ZnBr₂, ZnI₂, ZnCl₂, ZnSO₄, CuCl₂, CuCl, Cu(O₂)₃SCF₃, CoCl₂, CoI₂, FeI₂, FeCl₃, FeCl₂, FeCl₂(THF), FeCl₂, TiCl₄, TiCl₃, MnCl₂, ScCl₃, AlCl₃, (C₂H₅CH₂)₂AlCl₂, (C₂H₅CH₂)₂AlCl₂, Ph₂AlCl₂, PhAlCl₂, ReCl₅, ZrCl₄, NbCl₅, VCl₃, CrCl₃, MoCl₅, YCl₃.

CdCl₂.sub.2, LaCl₃.sub.3, Er(O₂.sub.3SCF₃.sub.3).sub.3, Yb(O₂.sub.2CCF₃.sub.3).sub.3, SmCl₃.sub.3, B(C₂.sub.6H₂.sub.5).sub.3, TaCl₅.sub.3. Suitable promoters known in the art. These include metal salts, such as ZnCl₂.sub.2, CoI₂.sub.2, and SnCl₂.sub.2, and organometallic compounds (such as R₂.sub.8AlCl₃.sub.2, R₂.sub.8SnO₂.sub.3SCF₃.sub.3, and R₂.sub.8B, where R₂.sub.8 is an alkyl or aryl group). U.S. Pat. No. 4,874,884 (incorporated herein by reference) describes how synergistic combinations of promoters can be chosen to increase the catalytic activity of the catalyst system. Preferred promoters include CdCl₂.sub.2, FeCl₂.sub.2, ZnCl₂.sub.2, B(C₂.sub.6H₂.sub.5).sub.3, and (C₂.sub.6H₂.sub.5).sub.3Sn(CF₃.sub.2).sub.3, CH₂.sub.3C₂.sub.6H₂.sub.5SO₂.sub.3, or (C₂.sub.6H₂.sub.5).sub.3BCN. The mole ratio of promoter to Group VIII metal present in the reaction can be within the range of about 1:16 to about 50:1.

SUMM [0038] The catalyst compositions of the present invention may also be used in the isomerization of allylic nitrites. The catalyst composition is combined with the allylic nitrile in a vessel and the isomerization process is carried at from 0 degrees C. to 150 degrees C., and preferably from 80 degrees C. to 120 degrees C. A solvent may be used. Examples of a suitable solvent include but are not limited to, hydrocarbons such as benzene, xylene, or combinations thereof; ethers such as tetrahydrofuran (THF); nitrites such as acetonitrile, benzonitrile, adiponitrile, or combinations of two or more thereof.

DETD [0039] The following non-limiting, representative examples illustrate the process and catalyst compositions of this invention. All parts, proportions, and percentages are by weight, unless otherwise indicated. In each example, the following procedure was used unless otherwise noted.

DETD [0040] Catalyst solutions were prepared by mixing one of the bidentate ligands of the invention and Ni(COD).sub.2 in a molar ratio of 1.1:1 and dissolving this in toluene. To the catalyst solution was added a solution of the promoter in the trans-3PN. The promoter: nickel molar ratio is 1.1:1. The molar ratio of trans-3PN to Ni was 200 equivalents. The reaction vessel was heated to the temperature as described in the following Tables and hydrogen cyanide was delivered by slow evaporation of the hydrogen cyanide from a reservoir connected to the reaction vessel by a feed tube in an otherwise closed reaction system. The reaction was analyzed after 15 hours. The reaction mixture was analyzed using standard Gas Chromatograph methodology. Tables I-through III list the conversion of pentenenitriles to dinitriles and the selectivity to adiponitrile, defined as the ratio of adiponitrile over all dinitriles, in this hydrocyanation reaction.

TABLE I

| Promoter: | ZnCl ₂ .sub.2 | Conversion to | Selectivity to |
|-----------|--------------------------|---------------|----------------|
| | | ligand | Dinitrile |
| | | | ADN |

50° C.

| | | |
|-----------|----------|------|
| Example 1 | ##STR6## | |
| | 73.8 | 91.0 |

| | | |
|-----------|----------|------|
| Example 2 | ##STR7## | |
| | 2.2 | 81.8 |

| | | |
|-----------|-----------|------|
| Example 3 | ##STR8## | |
| 57.4 | | 90.6 |
| Example 4 | ##STR9## | |
| 32.7 | | 87.6 |
| Example 5 | ##STR10## | |
| 87.5 | | 88.7 |
| Example 6 | ##STR11## | |
| 28.2 | | 85.1 |

80° C.

| | | |
|-----------|-----------|------|
| Example 7 | ##STR12## | |
| 13.5 | | 82.9 |
| Example 8 | ##STR13## | |
| 58.8 | | 73.0 |
| Example 9 | ##STR14## | |
| 66.0 | | 77.2 |

| | | |
|------------|-----------|------|
| Example 10 | ##STR15## | |
| 83.2 | | 73.7 |

DETD [0045] Catalyst Solution: For a typical multidentate phosphonite ligand 13 mmol of the bidentate ligand and 10 mmol of Ni(COD).sub.2 were combined in toluene to generate 3 g of catalyst solution.

DETD [0047] To a reaction vessel were added 0.1 ml of the catalyst solution. To this was added 0.18 g of the butadiene solution followed by 0.14 g of the HCN solution. The vessel was sealed and placed in a reactor set at 100° C. Samples were removed after three hours.

1. A hydrocyanation process, said process comprising: contacting an ethylenically unsaturated olefin compound with HCN in the presence of a catalyst composition, wherein said catalyst composition comprises a Group VIII metal and a phosphonite ligand wherein the ligand having a structure selected from the group consisting of: ##STR28## wherein the X groups are either the same or different unbridged organic aromatic groups as described in Formula I, wherein Q is a substituted or unsubstituted divalent aromatic or non aromatic hydrocarbon radical. The substituent on the Q groups is independently selected from the group consisting of C1 to C12 alkyl, cycloalkyl, alkoxy, alkylaryl, aryl, hetero aryl, cyano

10. The use of a catalyst based on a ligand of structure II for the hydrocyanation and/or the positional isomerization or double bond isomerization of olefins.

- IT 111-69-3P, Adiponitrile 592-51-8P, 4-Pentenenitrile 1635-87-4P , 3-Pentenenitrile 16545-78-1P, cis-3-Pentenenitrile (phosphonite ligands and their use in hydrocyanation)
- IT 16529-56-9P, 2-Methyl-3-butenenitrile 16529-66-1P, trans-3-Pentenenitrile (phosphonite ligands and their use in hydrocyanation)
- IT 74-90-8, Hydrogen cyanide, reactions 106-99-0, 1,3-Butadiene, reactions (phosphonite ligands and their use in hydrocyanation)
- IT 4635-87-4P, 3-Pentenenitrile 16545-78-1P, cis-3-Pentenenitrile (phosphonite ligands and their use in hydrocyanation)

10/586490

RN 4635-87-4 USPATFULL
CN 3-Pentenenitrile (CA INDEX NAME)



RN 16545-78-1 USPATFULL
CN 3-Pentenenitrile, (3Z)- (CA INDEX NAME)

Double bond geometry as shown.



IT 16529-66-1P, trans-3-Pentenenitrile
(phosphonite ligands and their use in hydrocyanation)
RN 16529-66-1 USPATFULL
CN 3-Pentenenitrile, (3E)- (CA INDEX NAME)

Double bond geometry as shown.



IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,
1,3-Butadiene, reactions
(phosphonite ligands and their use in hydrocyanation)
RN 74-90-8 USPATFULL
CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 USPATFULL
CN 1,3-Butadiene (CA INDEX NAME)



L88 ANSWER 50 OF 60 USPATFULL on STN
ACCESSION NUMBER: 2003:277344 USPATFULL Full-text
TITLE: PHOSPHONITE LIGANDS AND THEIR USE IN HYDROCYANATION

INVENTOR(S): Lenges, Christian P., Wilmington, DE, UNITED STATES
 Ritter, Joachim C., Wilmington, DE, UNITED STATES

| | NUMBER | KIND | DATE | |
|--|--|------|----------|------|
| PATENT INFORMATION: | US 2003195371 | A1 | 20031016 | <-- |
| | US 6660877 | B2 | 20031209 | |
| APPLICATION INFO.: | US 2002-93655 | A1 | 20020307 | (10) |
| DOCUMENT TYPE: | Utility | | | |
| FILE SEGMENT: | APPLICATION | | | |
| LEGAL REPRESENTATIVE: | E I DU PONT DE NEMOURS AND COMPANY, LEGAL PATENT RECORDS CENTER, BARLEY MILL PLAZA 25/1128, 4417 LANCASTER PIKE, WILMINGTON, DE, 19805 | | | |
| NUMBER OF CLAIMS: | 10 | | | |
| EXEMPLARY CLAIM: | 1 | | | |
| LINE COUNT: | 444 | | | |
| CAS INDEXING IS AVAILABLE FOR THIS PATENT. | | | | |
| AB | Disclosed herein are processes for hydrocyanation and isomerization of olefins by using at least one multidentate phosphonite ligands, including organometallic phosphonite ligands with a Group VIII metal or Group VIII metal compound, and optionally, a Lewis acid promoter. | | | |

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

SUMM [0001] The present invention concerns the use of catalyst compositions comprising a Group VIII metal and a multidentate phosphonite ligand for olefinic hydrocyanation and isomerization processes.

SUMM [0002] Certain phosphonites have been used as a part of hydrocyanation catalyst systems. U.S. Pat. No. 5,817,850 discloses the use of a catalyst composition in hydroformylation and hydrocyanation reactions. WO9843935 discloses the use of certain phosphonite ligands as part of a catalyst system in a process for producing an aldehyde. WO9946044 relates to a hydroformylation process using phosphonite ligands as part of the catalyst system for hydroformylation reactions. U.S. Pat. No. 6,242,633 discloses a process for the production of nitriles using catalysts containing phosphonite ligands. Further, WO9964155 discloses use of catalysts containing phosphorous ligands in hydrocyanation reactions.

SUMM [0003] Despite the disclosure of various ligands in hydrocyanation and hydroformylation processes. Catalyst compositions comprising certain multidentate phosphonite ligands show effectiveness and/or higher performance and achieve improvements in rapidity, selectivity, efficiency or stability.

SUMM [0004] A hydrocyanation process, said process comprising: contacting an ethylenically unsaturated olefin compound with HCN in the presence of a catalyst composition, wherein said catalyst composition comprises a Group VIII metal and a phosphonite ligand wherein the ligand having a structure selected from the group. . .

SUMM [0008] The use of a catalyst based on a ligand of structures I, II and III for the hydrocyanation and/or the positional isomerization or double bond. . .

SUMM . . . present invention describes a hydrocyanation process comprising: contacting an ethylenically unsaturated olefin compound with HCN in the presence of a catalyst composition, wherein the catalyst composition comprises a Group VIII metal and a phosphonite ligand having a structure selected from the group consisting of: ##STR4##

SUMM [0014] The hydrocyanation process described herein may be carried out in the presence of a catalyst precursor composition comprising a Group VIII metal and at least one multidentate phosphonite ligand having a structure I, II or. . .

SUMM . . . a compound thereof is combined with at least one of the ligand structures I, II or III to provide the catalyst. Among the Group VIII metal compounds, nickel, cobalt, and palladium compounds are preferred for hydrocyanation catalysts. A nickel compound is more preferred, and a zero-valent nickel compound having a ligand that can be chemically displaced by. . .

SUMM [0016] Zero-valent nickel compounds that can be used for preparing the catalyst of the present invention are disclosed in the art. The preferred zero-valent nickel compounds are Ni(COD).sub.2 (COD is 1,5-cyclooctadiene), Ni(P(O-O-C.sub.6H.sub.4CH.sub.3).sub.3).sub.3. . .

SUMM [0017] The catalyst of the present invention is prepared by combining the zero-valent nickel compound with at least one molar equivalent of the. . . of two or more thereof. The unsaturated olefin used in the hydrocyanation process may itself serve as the solvent. The catalyst preparation may be done at room temperature, or at a temperature that is appropriate for the solvent being used, or. . .

SUMM . . . at a temperature that is appropriate for the solvent being used, or the hydrocyanation process conditions being used. The resulting catalyst composition may be isolated, if desired.

SUMM [0021] The catalyst compositions of the present invention may be used with or without a Lewis acid in the hydrocyanation of organic compounds. The hydrocyanation process comprises contacting, in the presence of the catalyst, an olefinic unsaturated organic compound with a hydrogen cyanide-containing fluid under conditions sufficient to produce a nitrile, wherein the catalyst comprises a Group VIII metal, at least one of the ligands described above, and optionally a Lewis acid as a. . .

SUMM . . . a combination thereof. The hydrocyanation process can be carried out, for example, by charging a suitable vessel with an olefin, catalyst composition, and solvent, if used, to form a reaction mixture. Hydrogen cyanide can be combined initially with other components to. . .

SUMM [0023] Another suitable technique is to charge the vessel with the catalyst and the solvent (if any) to be used, and feed both the unsaturated compound and the HCN slowly to the. . .

SUMM [0024] The molar ratio of ethylenically unsaturated olefin compound to catalyst can be varied from about 10:1 to about 10000:1. The molar ratio of HCN to catalyst generally is varied from about 10:1 to 100,000:1, preferably 100:1 to 5,000:1, for a batch operation. In a continuous operation, such as when using a fixed bed catalyst type of operation, a higher proportion of catalyst can be used such as a molar ratio of about 5:1 to about 100,000:1, and preferably about 100:1 to about 5,000:1, HCN to catalyst.

SUMM . . . The solvent, if used, can be liquid at the reaction temperature and pressure and inert towards the olefin and the catalyst. Suitable solvents include, but are not limited to, hydrocarbons such as benzene, xylene, or combinations thereof; ethers such as tetrahydrofuran. . .

SUMM [0027] The exact temperature is dependent to a certain extent on the particular catalyst being used, the particular olefin being used and the desired reaction rate. Normally, temperatures of from about -25° C. to. . .

SUMM . . . in the presence of one or more Lewis acid promoters to affect both the activity and the selectivity of the catalyst system. The promoter may comprise an inorganic or organometallic compound in which the cation is selected from the group consisting. . . U.S. Pat. No. 4,874,884 (incorporated herein by reference) describes how synergistic combinations of promoters can be chosen to increase the catalytic activity of the catalyst system. Preferred promoters include CdCl₂.sub.2, FeCl₂.sub.2, ZnCl₂.sub.2, B(C₆H₅).sub.3, and

- (C._{sub.}6H._{sub.}5)._{sub.}3Sn(CF._{sub.}3SO._{sub.}3), CH._{sub.}3C._{sub.}6H._{sub.}5SO._{sub.}3, or (C._{sub.}6H._{sub.}5)._{sub.}3BCN. The mole ratio of promoter to Group . . .
- SUMM [0041] The catalyst compositions of the present invention may also be used in the isomerization of allylic nitrites. The catalyst composition is combined with the allylic nitrile in a vessel and the isomerization process is carried at from 0 degrees. . .
- DETD [0042] The following non-limiting, representative examples illustrate the process and catalyst compositions of this invention. All parts, proportions, and percentages are by weight, unless otherwise indicated. In each example, the following. . .
- DETD [0043] Catalyst solutions were prepared by mixing one of the bidentate ligands of the invention and Ni(COD)._{sub.}2 in a molar ratio of 1.1:1 and dissolving this in toluene. To the catalyst solution was added a solution of the promoter in the trans-3PN. The promoter: nickel molar ratio is 1.1:1. The molar. . .
- DETD [0048] Catalyst Solution: For a typical multidentate phosphonite ligand 13 mmol of the bidentate ligand and 10 mmol of Ni(COD)._{sub.}2 were combined in toluene to generate 3 g of catalyst solution.
- DETD [0050] To a reaction vessel were added 0.1 ml of the catalyst solution. To this was added 0.18 g of the butadiene solution followed by 0.14g of the HCN solution. The vessel. . .
- CLM What is claimed is:
- 1. A hydrocyanation process, said process comprising: contacting an ethylenically unsaturated olefin compound with HCN in the presence of a catalyst composition, wherein said catalyst composition comprises a Group VIII metal and a phosphonite ligand wherein the ligand having a structure selected from the group. . .
 - 10. The use of a catalyst based on a ligand of structures I, II and III for the hydrocyanation and/or the positional isomerization or double bond. . .
- IT 111-69-3P, Adiponitrile 592-51-8P, 4-Pentenenitrile 4635-87-4P , 3-Pentenenitrile 16545-78-1P, cis-3-Pentenenitrile (phosphonite ligands and their use in hydrocyanation)
- IT 16529-56-9P, 2-Methyl-3-butenenitrile 16529-66-1P, trans-3-Pentenenitrile (phosphonite ligands and their use in hydrocyanation)
- IT 74-90-8, Hydrogen cyanide, reactions 106-99-0, 1,3-Butadiene, reactions (phosphonite ligands and their use in hydrocyanation)
- PI US 2003195371 Al 20031016 <--| US 6660877 B2 200312091
- SUMM [0001] The present invention concerns the use of catalyst compositions comprising a Group VIII metal and a multidentate phosphonite ligand for olefinic hydrocyanation and isomerization processes.
- SUMM [0002] Certain phosphonites have been used as a part of hydrocyanation catalyst systems. U.S. Pat. No. 5,817,850 discloses the use of a catalyst composition in hydroformylation and hydrocyanation reactions. WO9843935 discloses the use of certain phosphonite ligands as part of a catalyst system in a process for producing an aldehyde. WO9946044 relates to a hydroformylation process using phosphonite ligands as part of the catalyst system for hydroformylation reactions. U.S. Pat. No. 6,242,633 discloses a process for the production of nitriles using catalysts containing phosphonite ligands. Further, WO9964155 discloses use of catalysts containing phosphorous ligands in hydrocyanation reactions.
- SUMM [0003] Despite the disclosure of various ligands in hydrocyanation and hydroformylation processes. Catalyst compositions comprising certain

multidentate phosphonite ligands show effectiveness and/or higher performance and achieve improvements in rapidity, selectivity, efficiency or stability.

- SUMM [0004] A hydrocyanation process, said process comprising: contacting an ethylenically unsaturated olefin compound with HCN in the presence of a catalyst composition, wherein said catalyst composition comprises a Group VIII metal and a phosphonite ligand wherein the ligand having a structure selected from the group consisting of: ##STR1##
- SUMM [0008] The use of a catalyst based on a ligand of structures I, II and III for the hydrocyanation and/or the positional isomerization or double bond isomerization of olefins.
- SUMM [0009] The present invention describes a hydrocyanation process comprising: contacting an ethylenically unsaturated olefin compound with HCN in the presence of a catalyst composition, wherein the catalyst composition comprises a Group VIII metal and a phosphonite ligand having a structure selected from the group consisting of: ##STR4##
- SUMM [0014] The hydrocyanation process described herein may be carried out in the presence of a catalyst precursor composition comprising a Group VIII metal and at least one multidentate phosphonite ligand having a structure I, II or III as described above and optionally a Lewis acid.
- SUMM [0015] Generally, a Group VIII metal or a compound thereof is combined with at least one of the ligand structures I, II or III to provide the catalyst. Among the Group VIII metal compounds, nickel, cobalt, and palladium compounds are preferred for hydrocyanation catalysts. A nickel compound is more preferred, and a zero-valent nickel compound having a ligand that can be chemically displaced by the ligand structure of the present invention is the most preferred source of Group VIII metal or Group VIII metal compound.
- SUMM [0016] Zero-valent nickel compounds that can be used for preparing the catalyst of the present invention are disclosed in the art. The preferred zero-valent nickel compounds are Ni(COD).sub.2 (COD is 1,5-cyclooctadiene), Ni{P(O-o-C.sub.6H.sub.4CH.sub.3).sub.3}.sub.3 and Ni{P(O-o-C.sub.6H.sub.4CH.sub.3).sub.3}.sub.2(C.sub.6H.sub.4CH.sub.3), all of which are known in the art.
- SUMM [0017] The catalyst of the present invention is prepared by combining the zero-valent nickel compound with at least one molar equivalent of the ligand of structure I, II or III of the present invention in a ratio of nickel:bidentate ligand of 1:1. The ligand may be combined with nickel in a solvent, or preferably in the substrate medium. Suitable solvents include, but are not limited to, hydrocarbons such as benzene, xylene, or combinations thereof; ethers such as tetrahydrofuran (THF); nitriles such as acetonitrile, benzonitrile, adiponitrile, or combinations of two or more thereof. The unsaturated olefin used in the hydrocyanation process may itself serve as the solvent. The catalyst preparation may be done at room temperature, or at a temperature that is appropriate for the solvent being used, or the hydrocyanation process conditions.
- SUMM [0019] The divalent nickel compound is combined with the ligand structure I, II or III of the present invention in a suitable solvent, preferably the unsaturated olefin, in a ratio of 1:1, or preferably at least 2:1. The combination is then combined with a suitable reducing agent at room temperature, or at a temperature that is appropriate for

the solvent being used, or the hydrocyanation process conditions being used. The resulting catalyst composition may be isolated, if desired.

- SUMM [0021] The catalyst compositions of the present invention may be used with or without a Lewis acid in the hydrocyanation of organic compounds. The hydrocyanation process comprises contacting, in the presence of the catalyst, an olefinic unsaturated organic compound with a hydrogen cyanide-containing fluid under conditions sufficient to produce a nitrile, wherein the catalyst comprises a Group VIII metal, at least one of the ligands described above, and optionally a Lewis acid as a promoter. As used herein, the term "fluid" means gas, a liquid, or a combination of these. Any fluid containing about 1 to 100% HCN can be used.
- SUMM [0022] A particularly significant use of the ligands of the present invention is in the hydrocyanation of olefins. In such a process, an olefinic compound such as a diolefinic compound can be converted to a nitrile or a dinitrile, or a combination thereof. The hydrocyanation process can be carried out, for example, by charging a suitable vessel with an olefin, catalyst composition, and solvent, if used, to form a reaction mixture. Hydrogen cyanide can be combined initially with other components to form the mixture. However, it is preferred that HCN be added slowly to the mixture after other components have been combined. Hydrogen cyanide can be delivered as a liquid or as a vapor to the vessel. As an alternative, a cyanohydrin can be used as the source of HCN. See, for example, U.S. Pat. No. 3,655,723, incorporated herein by reference.
- SUMM [0023] Another suitable technique is to charge the vessel with the catalyst and the solvent (if any) to be used, and feed both the unsaturated compound and the HCN slowly to the reaction mixture.
- SUMM [0024] The molar ratio of ethylenically unsaturated olefin compound to catalyst can be varied from about 10:1 to about 10000:1. The molar ratio of HCN to catalyst generally is varied from about 10:1 to 100,000:1, preferably 100:1 to 5,000:1, for a batch operation. In a continuous operation, such as when using a fixed bed catalyst type of operation, a higher proportion of catalyst can be used such as a molar ratio of about 5:1 to about 100,000:1, and preferably about 100:1 to about 5,000:1, HCN to catalyst.
- SUMM [0026] The hydrocyanation can be carried out with or without a solvent. The solvent, if used, can be liquid at the reaction temperature and pressure and inert towards the olefin and the catalyst. Suitable solvents include, but are not limited to, hydrocarbons such as benzene, xylene, or combinations thereof; ethers such as tetrahydrofuran (THF); nitriles such as acetonitrile, benzonitrile, adiponitrile, or combinations of two or more thereof. The unsaturated olefin to be hydrocyanated can itself serve as the solvent. Hydrocyanation can also be carried out in the gas phase.
- SUMM [0027] The exact temperature is dependent to a certain extent on the particular catalyst being used, the particular olefin being used and the desired reaction rate. Normally, temperatures of from about -25° C. to about 200° C. can be used with the range of 0° C. to 150° C. being preferred.
- SUMM [0035] The process of this invention can be carried out in the presence of one or more Lewis acid promoters to affect both the activity and the selectivity of the catalyst system. The promoter may comprise an

inorganic or organometallic compound in which the cation is selected from the group consisting of scandium, titanium, vanadium, chromium, manganese, iron, cobalt, copper, zinc, boron, aluminum, yttrium, zirconium, niobium, molybdenum, cadmium, rhenium and tin. Examples include, but are not limited to, ZnBr₂, ZnI₂, ZnCl₂, ZnSO₄, CuCl₂, CuI, Cu(O₂SCF₂)₂, CoCl₂, CoI₂, FeI₂, FeCl₂, FeCl₃, FeCl₂, FeCl₂(THF)₂, TiCl₂, TiCl₃, TiCl₄(THF)₂, MnCl₂, ScCl₂, AlCl₃, (C₂H₅OH)₂AlCl₃, (C₂H₅OH)₂AlCl₃, (iso-C₂H₅OH)₂AlCl₃, Ph₂AlCl₃, PhAlCl₂, ReCl₅, ZrCl₄, NbCl₅, VCl₃, CrCl₃, MOCl₅, YCl₃, CdCl₂, LaCl₃, Er(O₂SCF₂)₃, Yb(O₂CCF₃)₃, SmCl₃, B(C₂H₅OH)₅, TaCl₅. Suitable promoters known in the art. These include metal salts, such as ZnCl₂, CoI₂, and SnCl₂, and organometallic compounds (such as R₂AlCl₂, R₂SnO₂SCF₃, and R₂B₂, where R₂ is an alkyl or aryl group). U.S. Pat. No. 4,874,884 (incorporated herein by reference) describes how synergistic combinations of promoters can be chosen to increase the catalytic activity of the catalyst system. Preferred promoters include CdCl₂, FeCl₂, ZnCl₂, B(C₂H₅OH)₅, and (C₂H₅OH)₂Sn(CF₃SO₃), CH₂=CH₂, CH₂=CHCO₂R, or (C₂H₅OH)₂BCN. The mole ratio of promoter to Group VIII metal present in the reaction can be within the range of about 1:16 to about 50:1.

SUMM [0041] The catalyst compositions of the present invention may also be used in the isomerization of allylic nitrites. The catalyst composition is combined with the allylic nitrile in a vessel and the isomerization process is carried at from 0 degrees C. to 150 degrees C., and preferably from 80 degrees C. to 120 degrees C. A solvent may be used. Examples of a suitable solvent include but are not limited to, hydrocarbons such as benzene, xylene, or combinations thereof; ethers such as tetrahydrofuran (THF); nitriles such as acetonitrile, benzonitrile, adiponitrile, or combinations of two or more thereof.

DETD [0042] The following non-limiting, representative examples illustrate the process and catalyst compositions of this invention. All parts, proportions, and percentages are by weight, unless otherwise indicated. In each example, the following procedure was used unless otherwise noted.

DETD [0043] Catalyst solutions were prepared by mixing one of the bidentate ligands of the invention and Ni(COD)₂ in a molar ratio of 1:1 and dissolving this in toluene. To the catalyst solution was added a solution of the promoter in the trans-3PN. The promoter: nickel molar ratio is 1:1:1. The molar ratio of trans-3PN to Ni was 200 equivalents. The reaction vessel was heated to the temperature as described in the following Tables and hydrogen cyanide was delivered by slow evaporation of the hydrogen cyanide from a reservoir connected to the reaction vessel by a feed tube in an otherwise closed reaction system. The reaction was analyzed after 15 hours. The reaction mixture was analyzed using standard Gas Chromatograph methodology. Tables I-through III list the conversion of pentenenitriles to dinitriles and the selectivity to adiponitrile, defined as the ratio of adiponitrile over all dinitriles, in this hydrocyanation reaction.

TABLE I

Promoter: ZnCl₂
Conversion to Selectivity to

| ligand | ADN |
|-----------|-----|
| Dinitrile | ADN |

50° C.

| | | |
|-----------|-----------|--|
| Example 1 | ##STR11## | |
| 73.8 | 91.0 | |
| Example 2 | ##STR12## | |
| 2.2 | 81.8 | |
| Example 3 | ##STR13## | |
| 57.4 | 90.6 | |
| Example 4 | ##STR14## | |
| 32.7 | 87.6 | |
| Example 5 | ##STR15## | |
| 87.5 | 88.7 | |
| Example 6 | ##STR16## | |
| 28.2 | 85.1 | |

80° C.

| | | |
|-----------|-----------|--|
| Example 7 | ##STR17## | |
| 13.5 | 82.9 | |
| Example 8 | ##STR18## | |
| 58.8 | 73.0 | |
| Example 9 | ##STR19## | |
| 66.0 | 77.2 | |

| | | |
|------------|-----------|--|
| Example 10 | ##STR20## | |
| 83.2 | 73.7 | |

DETD [0048] Catalyst Solution: For a typical multidentate phosphonite ligand 13 mmol of the bidentate ligand and 10 mmol of Ni(COD).sub.2 were combined in toluene to generate 3 g of catalyst solution.

DETD [0050] To a reaction vessel were added 0.1 ml of the catalyst solution. To this was added 0.18 g of the butadiene solution followed by 0.14g of the HCN solution. The vessel was sealed and placed in a reactor set at 100° C. Samples were removed after three hours.

1. A hydrocyanation process, said process comprising: contacting an ethylenically unsaturated olefin compound with HCN in the presence of a catalyst composition, wherein said catalyst composition comprises a Group VIII metal and a phosphonite ligand wherein the ligand having a structure selected from the group consisting of: ##STR33## wherein the X groups can be independently chosen to be either a substituted or unsubstituted organic aromatic group. The substituent on the X groups is independently selected from the group consisting of C1 to C12 alkyl, perfluoroalkyl, cycloalkyl, alkoxy, acetal, ketal, alkylaryl, aryl, hetero aryl, cyano, and hydrogen. ##STR34## wherein the X groups are either the same or different unbridged organic aromatic groups as described in Formula I, wherein Q is a substituted or unsubstituted divalent aromatic or non aromatic hydrocarbon radical. The 25 substituent on the Q groups is independently selected from the group consisting of C1 to C12 alkyl, cycloalkyl, alkoxy, alkylaryl, aryl, hetero aryl, cyano. ##STR35## wherein X and Q are as described in Formula II, and L is a linking group selected from the group consisting

of --CR₁R₂-, --O--, --S--, --CO-- (wherein each of R₁-R₂ are independent of one another, are a hydrogen atom, a C1-12 alkyl group, or an aryl group), and each of m and m' which are independent of each other, are 0 or 1.

10. The use of a catalyst based on a ligand of structures I, II and III for the hydrocyanation and/or the positional isomerization or double bond isomerization of olefins.

- IT 111-69-3P, Adiponitrile 592-51-8P, 4-Pentenenitrile 4635-87-4P
, 3-Pentenenitrile 16545-78-1P, cis-3-Pentenenitrile
(phosphonite ligands and their use in hydrocyanation)
IT 16529-56-9P, 2-Methyl-3-butenenitrile 16529-66-1P,
trans-3-Pentenenitrile
(phosphonite ligands and their use in hydrocyanation)
IT 74-90-8, Hydrogen cyanide, reactions 106-99-8,
1,3-Butadiene, reactions
(phosphonite ligands and their use in hydrocyanation)
IT 4635-87-4P, 3-Pentenenitrile 16545-78-1P,
cis-3-Pentenenitrile
(phosphonite ligands and their use in hydrocyanation)
RN 4635-87-4 USPATFULL
CN 3-Pentenenitrile (CA INDEX NAME)



- RN 16545-78-1 USPATFULL
CN 3-Pentenenitrile, (3Z)- (CA INDEX NAME)

Double bond geometry as shown.



- IT 16529-66-1P, trans-3-Pentenenitrile
(phosphonite ligands and their use in hydrocyanation)
RN 16529-66-1 USPATFULL
CN 3-Pentenenitrile, (3E)- (CA INDEX NAME)

Double bond geometry as shown.



- IT 74-90-8, Hydrogen cyanide, reactions 106-99-8,
1,3-Butadiene, reactions
(phosphonite ligands and their use in hydrocyanation)
RN 74-90-8 USPATFULL
CN Hydrocyanic acid (CA INDEX NAME)

N
CH

RN 106-99-0 USPATFULL
 CN 1,3-Butadiene (CA INDEX NAME)



L88 ANSWER 51 OF 60 USPATFULL on STN
 ACCESSION NUMBER: 2003:220400 USPATFULL Full-text
 TITLE: Supported bis(phosphorus) ligands and their use in the
 catalysis
 INVENTOR(S): Cobb, Michael W., Wilmington, DE, UNITED STATES
 Qiu, Weiming, Wilmington, DE, UNITED STATES

| | NUMBER | KIND | DATE |
|---------------------|----------------|------|---------------|
| PATENT INFORMATION: | US 2003153691 | A1 | 20030814 |
| | US 6984604 | B2 | 20060110 |
| APPLICATION INFO.: | US 2002-305230 | A1 | 20021126 (10) |

| | NUMBER | DATE |
|-----------------------|--|---------------|
| PRIORITY INFORMATION: | US 2001-333365P | 20011126 (60) |
| DOCUMENT TYPE: | Utility | |
| FILE SEGMENT: | APPLICATION | |
| LEGAL REPRESENTATIVE: | E I DU PONT DE NEMOURS AND COMPANY, LEGAL PATENT RECORDS CENTER, BARLEY MILL PLAZA 25/1128, 4417 LANCASTER PIKE, WILMINGTON, DE, 19805 | |

NUMBER OF CLAIMS: 26
 EXEMPLARY CLAIM: 1
 LINE COUNT: 1383

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB Supported bis(phosphorus) ligands are disclosed for use in a variety of catalytic processes, including the isomerization, hydrogenation, hydroformylation, and hydrocyanation of unsaturated organic compounds. Catalysts are formed when the ligands are combined with a catalytically active metal, such as nickel.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

SUMM . . . The group X may contain from 1 to 50 carbon atoms. It may also optionally contain heteroatoms such as oxygen, nitrogen, halogen, and the like, and also functional groups such as ethers, alcohols, esters, amides, as well as others. The groups. . .

SUMM [0085] A non-oxidizing environment is desirable in order to retard oxidative deactivation of the catalyst. Accordingly, an inert atmosphere, e.g., nitrogen, is preferably used, although air can be used.

SUMM . . . unsaturated organic compound can also be substituted with one

or more functional groups containing a heteroatom, such as oxygen, sulfur, nitrogen or phosphorus. Examples of these heteroatom-substituted ethenically unsaturated organic compounds include vinyl methyl ether, methyl oleate, oleyl alcohol, 3-pentenenitrile, 4-pentenenitrile, . . .

SUMM . . . phase. A given catalyst is loaded into a reactor, such as a tubular reactor, taking care to avoid exposure of air-sensitive catalysts to oxygen from the air. A gaseous mixture of the desired olefinic compound, carbon monoxide and hydrogen, along with any desired diluent, such as nitrogen, helium or argon, is then passed through the reactor while contacting the catalyst. The reaction products are generally liquid at room temperature and . . .

DETD . . . above nickel catalyst, 19 mg of zinc chloride and 5 mL of 3-pentenenitrile. The hydrocyanation reaction was done at a nitrogen flow rate of 12 cc/min with the oil bath at 50°C. for 180 minutes and then 70°C. for . . .

IT 74-90-8, Hydrocyanic acid, reactions 106-99-0,
Butadiene, reactions 630-08-0, Carbon monoxide, reactions
4635-87-4, 3-Pentenenitrile 16529-56-9, 2-Methyl-3-
butenenitrile

(polymer supported bis(phosphorus)ligands and their use in catalysis)
SUMM [0067] Polymer-supported bis(phosphorus) ligands have been prepared by a variety of methods known in the art, for example, see descriptions in WO 93,03839; U.S. Pat. No. 4,769,498 and U.S. Pat. No. 4,668,651. In general, the transformation involves the reaction of a phosphorus halide, typically but not limited to chloride, with the diol to form P-O bonds. The phosphorus halide may be any compound of the type PY._nX_n.sub.3-n, where Y=halide, X=alkoxide, aryloxide, alkyl, aryl, and n=3, 2, or 1. The preferred phosphorus halides of the present invention are those where Y=Cl; X=alkoxide, aryloxide, alkyl, or aryl; and n=1. The group X may contain from 1 to 50 carbon atoms. It may also optionally contain heteroatoms such as oxygen, nitrogen, halogen, and the like, and also functional groups such as ethers, alcohols, esters, amides, as well as others. The groups X may or may not be linked to form a cyclic structure. The PX._n moiety may form a ring and X may also be alkoxide, aryloxide, alkyl, aryl, or a combination of them. Many dialkyl chlorophosphines and diaryl chlorophosphines are commercially available, or may be prepared by methods known in the art, for example, J. Am. Chem. Soc. 1994, 116, 9869. Phosphorochloridites, may be prepared by a variety of methods known in the art, for example, see descriptions in Polymer 1992, 33,161; Inorg. Syn. 1966, 8, 68; U.S. Pat. No. 5,210,260; Z. Anorg. Allg. Chem. 1986, 535, 221. For example, the reaction of 2,2'-biphenol with phosphorus trichloride gives 1,1'-biphenyl-2,2'-diylphosphorochloridite.

SUMM [0085] A non-oxidizing environment is desirable in order to retard oxidative deactivation of the catalyst. Accordingly, an inert atmosphere, e.g., nitrogen, is preferably used, although air can be used.

SUMM [0094] The unsaturated organic compound can also be substituted with one or more functional groups containing a heteroatom, such as oxygen, sulfur, nitrogen or phosphorus. Examples of these heteroatom-substituted ethenically unsaturated organic compounds include vinyl methyl ether, methyl oleate, oleyl alcohol, 3-pentenenitrile, 4-pentenenitrile, 3-pentenoic acid, 4-pentenoic acid, methyl 3-pentenoate, 7-octen-1-al, acrylonitrile, acrylic acid esters, methyl acrylate, methacrylic acid esters, methyl methacrylate, acrolein, allyl alcohol, 3-pentenal, 4-pentenal, and combinations of two or more thereof.

SUMM [0104] The hydroformylation process can be run in solution or in the gas phase. When the hydroformylation is carried out in the vapor phase, the preferred temperature range is from about 50° C. to about 180° C., most preferably from about 90° C. to 110° C. The temperature must be chosen so as to maintain all of the reactants and products in the vapor phase, but low enough to prevent deterioration of the catalyst. The particular preferred temperature depends to some extent on the catalyst being used, the olefinic compound being used, and the desired reaction rate. The operating pressure is not particularly critical and can be from about 0.101 to 1.01 MPa. The pressure and temperature combination must be chosen so as to maintain reactants and products in the vapor phase. A given catalyst is loaded into a reactor, such as a tubular reactor, taking care to avoid exposure of air-sensitive catalysts to oxygen from the air. A gaseous mixture of the desired olefinic compound, carbon monoxide and hydrogen, along with any desired diluent, such as nitrogen, helium or argon, is then passed through the reactor while contacting the catalyst. The reaction products are generally liquid at room temperature and are conveniently recovered by cooling. The reactor effluent can be directly connected to a sampling valve and can be analyzed by gas chromatography. Aldehydic products, such as linear and branched butyraldehydes obtained from hydroformylation of propylene, can be quantitatively separated and analyzed using a 30 M DB-Wax® capillary GC column.

DETD [0179] A three necked flask was charged with 0.284 g of the above nickel catalyst, 19 mg of zinc chloride and 5 mL of 3-pentenenitrile. The hydrocyanation reaction was done at a nitrogen flow rate of 12 cc/min with the oil bath at 50° C. for 180 minutes and then 70° C. for 120 minutes. GC analysis indicated 87% of the pentenenitriles have converted to dinitriles with an adiponitrile distribution of 93%.

IT 74-90-8, Hydrocyanic acid, reactions 106-99-0,
 Butadiene, reactions 630-08-0, Carbon monoxide, reactions
 4635-87-4, 3-Pentenenitrile 16529-56-9, 2-Methyl-3-
 butenenitrile

(polymer supported bis(phosphorus)ligands and their use in catalysis)

IT 74-90-8, Hydrocyanic acid, reactions 106-99-0,
 Butadiene, reactions 4635-87-4, 3-Pentenenitrile

(polymer supported bis(phosphorus)ligands and their use in catalysis)

RN 74-90-8 USPATFULL

CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 USPATFULL
 CN 1,3-Butadiene (CA INDEX NAME)



RN 4635-87-4 USPATFULL

CN 3-Pentenenitrile (CA INDEX NAME)



L88 ANSWER 52 OF 60 USPATFULL on STN

ACCESSION NUMBER: 20031208079 USPATFULL Full-text

TITLE: Phosphorus-containing compositions and their use in hydrocyanation, isomerization and hydroformylation reactions

INVENTOR(S): Gagne, Michel R., Carrboro, NC, UNITED STATES
 Moloy, Kenneth G., Hockessin, DE, UNITED STATES
 Radu, Nora S., Landenberg, PA, UNITED STATES
 Santora, Brian P., River Falls, WI, UNITED STATES
 Tam, Wilson, Boothwyn, PA, UNITED STATES

| | NUMBER | KIND | DATE |
|--|--|------|--------------|
| PATENT INFORMATION: | US 2003144440 | A1 | 20030731 |
| | US 6660876 | B2 | 20031209 |
| APPLICATION INFO.: | US 2001-994135 | A1 | 20011126 (9) |
| DOCUMENT TYPE: | Utility | | |
| FILE SEGMENT: | APPLICATION | | |
| LEGAL REPRESENTATIVE: | E I DU PONT DE NEMOURS AND COMPANY, LEGAL PATENT RECORDS CENTER, BARLEY MILL PLAZA 25/1128, 4417 LANCASTER PIKE, WILMINGTON, DE, 19805 | | |
| NUMBER OF CLAIMS: | 45 | | |
| EXEMPLARY CLAIM: | 1 | | |
| LINE COUNT: | 2482 | | |
| CAS INDEXING IS AVAILABLE FOR THIS PATENT. | | | |
| AB | A polymeric, phosphorus-containing composition made by heating, in the presence of an initiator, preferably a free radical initiator, and optionally in the presence of one or more comonomers, at least one substituted phosphonylated 2,2'-dihydroxyl-1,1'-binaphthalene or at least one substituted 2,2'-dihydroxyl-1,1'-biphenylene. | | |

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

DETD . . . unsaturated organic compound can also be substituted with one or more functional groups containing a heteroatom, such as oxygen, sulfur, nitrogen or phosphorus. Examples of these heteroatom-substituted, ethylenically unsaturated, organic compounds include vinyl methyl ether, methyl oleate, oleyl alcohol, 3-pentenenitrile, 4-pentenenitrile, . . .

DETD . . . into a reactor, such as a tubular reactor, taking care to avoid exposure of oxygen-sensitive catalysts to oxygen from the air. A gaseous mixture of the desired olefinic compound, carbon monoxide and hydrogen, along with any desired diluent, such as nitrogen, helium or argon, is then passed through the reactor while contacting the catalyst. The reaction products are generally liquid at room temperature and . . .

DETD . . . herein, a non-oxidizing environment is desirable in order to retard oxidative deactivation of the catalyst. Accordingly, an inert atmosphere, e.g., nitrogen, is preferably used, although air can be used, if desired, at the expense of loss of a proportion of the catalyst acitivity through oxidation. Impurities. . .

- DETD . . . in a thermostatically controlled oil bath. HCN was delivered to the flask as an HCN/N₂ gas mixture by bubbling dry nitrogen carrier gas through liquid HCN maintained in an ice bath at 0° C. This provided a vapor stream that was about 35% by volume HCN. The rate of nitrogen gas flow determined the rate of HCN delivery. Samples were periodically analyzed by gas chromatography (GC).
- DETD [0158] Aspect 2: Preparation of ethylenically unsaturated, phosphorus-containing bidentate ligand (1): Under nitrogen atmosphere, a 100 mL flask with magnetic stir bar was charged with 2.450 grams of 2,2-bis(4-hydroxy-3-methylphenyl)propane, 0.865 grams of acryloyl.
- DETD [0203] Aspect 2: Preparation of ethylenically unsaturated ligand (8): Under nitrogen, a 100 mL flask with magnetic stir bar was charged with 1.880 grams of 2,2-bis(4-hydroxy-3-methylphenyl)propane, 0.664 grams of acryloyl chloride, . . .
- DETD . . . and 5 mL of 3PN in a closed reactor was placed in a 50° C. oil bath and HCN saturated nitrogen was delivered at a nitrogen flow rate of 24 cc/min. The reaction was heated at 50° C. for 1 hour and then at 70° C. for 30 minutes. Nitrogen flow was decreased to 12 cc/min. and the reaction was run at 70° C. for an additional 90 minutes. The . . .
- DETD [0227] Aspect 2: Preparation of ethylenically unsaturated ligand (12): Under nitrogen, a 100 mL flask with magnetic stir bar was charged with 0.931 grams of the monoacrylate of 2,2-bis(4-hydroxy-3-methylphenyl)propane (prepared from. . .)
- DETD . . . to the mixture. The mixture was heated in a 50° C. oil bath and HCN was delivered with 24 cc/min. nitrogen flow rate. After 90 minutes of reaction, GC analysis indicated 57.6% conversion of 3PN with 92% selectivity to ADN. To. . . but the reaction was allowed to continue at 50° C. for 120 minutes. The mixture was allowed to sit under nitrogen at room temperature overnight. GC analysis indicated 62% conversion of 3PN with 91.3% selectivity to ADN.
- DETD . . . begin an additional reaction. The reaction was placed in a 70° C. oil bath and HCN was delivered with a nitrogen flow rate of 30 cc/min. The reaction was then stored at room temperature overnight. The mixture was then heated at 70° C. oil bath with HCN delivered with a nitrogen flow rate of 30 cc/min for 30 minutes. GC analysis indicated 75% conversion of 3PN with selectivity to ADN of. . . was added 5 mL of 3PN. The mixture was heated at 70° C. oil bath with HCN delivered with a nitrogen flow rate of 30 cc/min for 210 minutes. GC analysis indicated 65% conversion of 3PN with selectivity to ADN of. . .
- DETD [0243] Aspect 2: Preparation of the diphosphite ligand (13): Under an atmosphere of nitrogen, a cold (-30° C.) Et₂O (5 mL) solution of 6,6'-divinyl-2,2'-dihydroxy-1,1'-binaphthyl (0.051 g, 1.5×10⁻⁴ mol) and Et₂O (0.040, 3.9×10⁻⁴ mol) was. . .
- DETD [0244] Aspect 3: Polymerization of the ethylenically unsaturated compound (13) with divinylbenzene: Under an atmosphere of nitrogen, a vial fitted with a Teflon® fluoropolymer resin screwcap was charged with the diphosphite (0.027 g, 2.7×10⁻⁵ mol) described in. . .
- DETD [0247] Aspect 2: Preparation of ethylenically unsaturated diphosphite ligand (14): Under an atmosphere of nitrogen, a cold (-30° C.) Et₂O (5 mL) solution of 3,3',4,4',5,5',6,6'-octamethyl-2,2'-dihydroxy-1,1'-biphenyl (0.100 g, 0.67 mmol) and Et₂O (0.152 g, 1.5 mmol). . .
- DETD [0248] Aspect 3: Polymerization of the ethylenically unsaturated compound (14) with divinylbenzene and styrene: Under an atmosphere of

- nitrogen, a vial fitted with a Teflon® fluoropolymer resin screwcap was charged with the diphosphite (0.100 g, 0.09 mmol) described in. . .
- DETD [0251] Aspect 5.1: Polymerization of 6,6'-divinyl-2,2'-dihydroxy-1,1'-binaphthyl with styrene: Under nitrogen atmosphere, a vial fitted with a Teflon® fluoropolymer resin screwcap was charged with 6,6'-divinyl-2,2'-dihydroxy-1,1'-binaphthyl (0.500g, 1.48 mmol), AIBN (0.040 g),. . .
- DETD [0252] Aspect 5.2: Formation of the diphosphite ligand from the polymeric precursor of Example 15: Under nitrogen atmosphere, a cold solution (-30° C.) of o-cresol (0.027 g, 0.25 mmol) in toluene (5 mL) was added to a. . .
- DETD . . . mL of 3PN. The mixture was heated in a 70 C. oil bath and HCN was delivered with 12 cc/min. nitrogen flow rate. After 180 minutes, GC indicated 93.9% conversion to dinitrile with ADN selectivity of 88.4%.
- IT 106-99-0, Butadiene, reactions 4635-87-4,
3-Pentenenitrile
(hydrocyanation of; manufacture of unsatd. phosphorus-containing compns. and their use in hydrocyanation, isomerization and hydroformylation reactions)
- IT 74-85-1, Ethylene, reactions 74-90-8, Hydrogen cyanide, reactions 79-97-0, 2,2-Bis(4-hydroxy-3-methylphenyl)propane 814-68-6, Acryloyl chloride 7719-12-2, Phosphorus trichloride 13185-00-7, 6,6'-Dibromo-2,2'-dihydroxy-1,1'-binaphthyl 26567-10-2 31860-10-3 50291-18-4 100930-72-1 532941-08-5 538345-81-2 538346-27-9 538346-36-0
(manufacture of unsatd. phosphorus-containing compns. and their use in hydrocyanation, isomerization and hydroformylation reactions)
- DETD [0135] The unsaturated organic compound can also be substituted with one or more functional groups containing a heteroatom, such as oxygen, sulfur, nitrogen or phosphorus. Examples of these heteroatom-substituted, ethylenically unsaturated, organic compounds include vinyl methyl ether, methyl oleate, oleyl alcohol, 3-pentenenitrile, 4-pentenenitrile, 3-pentenoic acid, 4-pentenoic acid, methyl 3-pentenoate, 7-octen-1-al, acrylonitrile, acrylic acid esters, methyl acrylate, methacrylic acid esters, methyl methacrylate, acrolein, allyl alcohol, 3-pentenal, 4-pentenal, and combinations of two or more thereof.
- DETD [0144] The hydroformylation process can be run in solution or in the gas phase. When the hydroformylation is carried out in the vapor phase, the preferred temperature range is from about 50° C. to about 180° C., most preferably from about 90° C. to 110° C. The temperature must be chosen high enough so as to maintain all of the reactants and products in the vapor phase, but low enough to prevent deterioration of the catalyst. The particular preferred temperature depends to some extent on the catalyst being used, the olefinic compound being used, and the desired reaction rate. The operating pressure is not particularly critical and can be from about 0.1 to 1.0 MPa. The pressure and temperature combination must be chosen so as to maintain reactants and products in the vapor phase. A given catalyst is loaded into a reactor, such as a tubular reactor, taking care to avoid exposure of oxygen-sensitive catalysts to oxygen from the air. A gaseous mixture of the desired olefinic compound, carbon monoxide and hydrogen, along with any desired diluent, such as nitrogen, helium or argon, is then passed through the reactor while contacting the catalyst. The reaction products are generally liquid at room temperature and are conveniently recovered by cooling. The reactor effluent can be directly

- connected to a sampling valve and can be analyzed by gas chromatography. Aldehydic products, such as linear and branched butyraldehydes obtained from hydroformylation of propylene, can be quantitatively separated and analyzed using a 30M DB-Wax® capillary GC column.
- DETD [0145] For the hydrocyanation, isomerization, and hydroformylation processes described herein, a non-oxidizing environment is desirable in order to retard oxidative deactivation of the catalyst. Accordingly, an inert atmosphere, e.g., nitrogen, is preferably used, although air can be used, if desired, at the expense of loss of a proportion of the catalyst acitivity through oxidation. Impurities that are detrimental to the catalyst should be kept to a minimum.
- DETD [0156] Hydrocyanation of 3-pentenenitrile was also performed by slowly adding the HCN to the reaction mixture. The catalyst composition and 3-pentenenitrile were heated in a thermostatically controlled oil bath. HCN was delivered to the flask as an HCN/N₂ gas mixture by bubbling dry nitrogen carrier gas through liquid HCN maintained in an ice bath at 0° C. This provided a vapor stream that was about 35% by volume HCN. The rate of nitrogen gas flow determined the rate of HCN delivery. Samples were periodically analyzed by gas chromatography (GC).
- DETD [0158] Aspect 2: Preparation of ethylenically unsaturated, phosphorus-containing bidentate ligand (1): Under nitrogen atmosphere, a 100 mL flask with magnetic stir bar was charged with 2.450 grams of 2,2-bis(4-hydroxy-3-methylphenyl)propane, 0.865 grams of acryloyl chloride, 40 mL of toluene and 8 mL of THF. The mixture was cooled to -30° C. and 1.2 grams of triethylamine in 15 mL of toluene was added. About a quarter of the solvent was removed under vacuum and the mixture cooled to -30° C. To this mixture was added 2.266 grams of the phosphorodichloride of 2-isopropylphenol and 1.2 grams of triethylamine in 10 mL of toluene. The mixture was stirred for one and one-half hours and cooled to -30° C. To the mixture was added 1.157 grams of 3,3',5,5'-tetramethyl-2,2'-biphenol and 1.2 grams of triethylamine. The mixture was kept at -30° C. overnight and then filtered. Solvent was removed to give 5.978 grams of a tacky brown solid (.sup.31P NMR in CDCl₃.sub.3: 142.21, 142.15, 135.20, 135.11, 134.74, 134.29, 132.01, 131.96, and 131.13).
- DETD [0203] Aspect 2: Preparation of ethylenically unsaturated ligand (8): Under nitrogen, a 100 mL flask with magnetic stir bar was charged with 1.880 grams of 2,2-bis(4-hydroxy-3-methylphenyl)propane, 0.664 grams of acryloyl chloride, and 40 mL of THF. The mixture was cooled to -30° C. and a pre-cooled solution (at -30° C.) containing 1 gram of triethylamine in 15 mL of THF was added. The THF was removed under vacuum and the residue dissolved in 50 mL of THF. To this slurry was added 0.503 grams of phosphorus trichloride. The mixture was cooled to -30° C. and a pre-cooled solution containing 0.5 gram of triethylamine in 10 mL of THF was added. After stirring for several days, 0.598 grams of 3,3'-diisopropyl-5,5',6,6'-tetramethyl-2,2'-biphenol was added along with 1.2 grams of triethylamine. The mixture was stirred for forty minutes, filtered and the solvent was removed under vacuum to give 3.146 grams of a yellow solid (.sup.31P NMR (CDCl₃.sub.3): 135.58, 135.25, 135.18, 134.80, 134.71, 132.71, 131.90, 130.80, 127.94, and 127.87).
- DETD [0226] Aspect 10: Semibatch 3-pentenenitrile hydrocyanation using nickel catalyst: A reaction mixture of 0.567 grams of the above catalyst, 0.027 grams of zinc chloride, 5 mL of toluene and 5 mL of 3PN in a closed reactor was placed in a 50° C. oil bath and HCN saturated nitrogen was delivered at a nitrogen flow rate of 24 cc/min. The reaction was heated at 50° C. for 1 hour and then at 70° C. for 30 minutes. Nitrogen flow was decreased to 12 cc/min. and the reaction was run at 70° C. for an additional 90 minutes. The

- temperature was then increased to 80° C. and the reaction was continued for another 90 minutes. GC analysis indicated 68% conversion of 3-pentenenitrile to dinitrile with an ADN selectivity of 89%.
- DETD [0227] Aspect 2: Preparation of ethylenically unsaturated ligand (12): Under nitrogen, a 100 mL flask with magnetic stir bar was charged with 0.931 grams of the monoacrylate of 2,2-bis(4-hydroxy-3-methylphenyl)propane (prepared from the reaction of acryloyl chloride with 2,2-bis(4-hydroxy-3-methylphenyl)propane), 0.627 grams of the phosphorodichloridite of o-cresol, and 40 mL of toluene. The mixture was cooled to -30° C. and a precooled solution (at -30° C.) containing 0.4 grams of triethylamine in 15 mL of toluene was added. After stirring for 2 hours, .sup.31P NMR in CDCl₃.sub.3 indicated a peak at 162.8 ppm. The mixture was cooled to -30° C. and 0.448 grams of 3,3',4,4',5,5'-hexamethyl-2,2'-biphenol and 0.65 grams of triethylamine in 2 mL of THF were added. After stirring overnight, the mixture was filtered and the THF removed under vacuum to give a yellow solid. The solid was dissolved in 10 mL of toluene and 0.8 grams of triethylamine was added in 5 mL of THF. The mixture was stirred overnight and filtered. The solvent was removed. .sup.31P NMR indicated some phosphorodichloridite still present. The residue was dissolved in THF and 0.75 grams of triethylamine were added. After stirring overnight, the mixture was filtered through silica gel, and the solvent was removed under vacuum. 1.225 Grams of yellow solid were recovered (.sup.31P NMR in CDCl₃.sub.3: 137.47, 137.31, 135.29, 135.21, 135.15, 135.00, 134.82, 134.73, 134.40, 134.31, 133.41, 133.40, 132.07, 131.98, 130.44, 127.74, and 127.69).
- DETD [0235] Aspect 10: Hydrocyanation of 3-pentenenitrile: 29 milligrams of ZnCl₃.sub.2 and 5 mL of 3PN were added to the mixture. The mixture was heated in a 50° C. oil bath and HCN was delivered with 24 cc/min. nitrogen flow rate. After 90 minutes of reaction, GC analysis indicated 57.6% conversion of 3PN with 92% selectivity to ADN. To the mixture was added 5 mL of 3PN and the reaction was continued for 90 minutes. At this point, HCN delivery was stopped but the reaction was allowed to continue at 50° C. for 120 minutes. The mixture was allowed to sit under nitrogen at room temperature overnight. GC analysis indicated 62% conversion of 3PN with 91.3% selectivity to ADN.
- DETD [0236] Ligand recycle: At this time, the solvent was removed via syringe from the reactor. 5 mL of toluene, 5 mL of 3PN and 29 milligrams of ZnCl₃.sub.2 were added to begin an additional reaction. The reaction was placed in a 70° C. oil bath and HCN was delivered with a nitrogen flow rate of 30 cc/min. The reaction was then stored at room temperature overnight. The mixture was then heated at 70° C. oil bath with HCN delivered with a nitrogen flow rate of 30 cc/min for 30 minutes. GC analysis indicated 75% conversion of 3PN with selectivity to ADN of 92.2%. To this mixture was added 5 mL of 3PN. The mixture was heated at 70° C. oil bath with HCN delivered with a nitrogen flow rate of 30 cc/min for 210 minutes. GC analysis indicated 65% conversion of 3PN with selectivity to ADN of 91.8%.
- DETD [0243] Aspect 2: Preparation of the diphosphite ligand (13): Under an atmosphere of nitrogen, a cold (-30° C.) Et₃.sub.20 (5 mL) solution of 6,6'-divinyl-2,2'-dihydroxy-1,1'-binaphthyl (0.051 g, 1.5×10.sup.-4 mol) and Et₃.sub.3N (0.040, 3.9×10.sup.-4 mol) was slowly added to a Et₃.sub.20 (5 mL) solution of phosphorochloridite of 2-isopropoxyphenol (0.140 g, 3.9×10.sup.-4 mol). The solution was allowed to warm up to room temperature and was stirred for one hour. The reaction mixture was filtered through celite and alumina. The volatiles were evaporated to yield a white powder in 67% yield. (0.100 g).
- DETD [0244] Aspect 3: Polymerization of the ethylenically unsaturated

compound (13) with divinylbenzene: Under an atmosphere of nitrogen, a vial fitted with a Teflon® fluoropolymer resin screwcap was charged with the diphosphite (0.027 g, $2.7 \times 10.\text{sup}.\text{-}5$ mol) described in example 13, AIBN (0.002 g), DVB (0.1900 g) and THF (0.184 g). This vial was screwed shut and placed in a 70° C. oil bath for 24 hours.

After polymerization, the polymer was crushed and the volatiles were removed under vacuum. The resulting white polymer (0.350 g) was insoluble in all organic solvents. Elemental analysis: P found: 1.51%.

DETD [0247] Aspect 2: Preparation of ethylenically unsaturated diphosphite ligand (14): Under an atmosphere of nitrogen, a cold (-30° C.) Et.sub.20 (5 mL) solution of 3,3',4,4',5,5',6,6'-octamethyl-2,2'-dihydroxy-1,1'-biphenyl (0.100 g, 0.67 mmol) and Et.sub.3N (0.152 g, 1.5 mmol) was slowly added to an Et.sub.20 (5 mL) solution of phosphorochlorodite of trans-2-ethoxy-5-(1-propenyl)phenol (0.631 g, 1.5 mmol). The solution was allowed to warm to room temperature and was stirred for one hour. The reaction mixture was filtered through celite and alumina. The volatiles were evaporated to give 86% yield of a white powder (0.623 g).

DETD [0248] Aspect 3: Polymerization of the ethylenically unsaturated compound (14) with divinylbenzene and styrene: Under an atmosphere of nitrogen, a vial fitted with a Teflon® fluoropolymer resin screwcap was charged with the diphosphite (0.100 g, 0.09 mmol) described in example 14, AIBN (0.005 g), DVB (0.40 g), styrene (0.70 g) and THF (1.5 mL). This vial was screwed shut and placed in a 70° C. oil bath for 48 hours, after which DVB (0.75 g) and AIBN (0.005 g) were added and the vial was returned to the oil bath. After 48 hours, the opaque polymer was crushed and the volatiles were removed under vacuum. The resulting white polymer (0.137 g) was insoluble in all organic solvents.

DETD [0251] Aspect 5.1: Polymerization of 6,6'-divinyl-2,2'-dihydroxy-1,1'-binaphthyl with styrene: Under nitrogen atmosphere, a vial fitted with a Teflon® fluoropolymer resin screwcap was charged with 6,6'-divinyl-2,2'-dihydroxy-1,1'-binaphthyl (0.500g, 1.48 mmol), AIBN (0.040 g), styrene (4.0 mL) and THF (4.0 mL). The vial was screwed shut and placed in a 70° C. oil bath for 24 hours. After polymerization, the polymer was crushed and the volatiles were removed under vacuum. The resulting white polymer (4.8 g) was insoluble in all organic solvents.

DETD [0252] Aspect 5.2: Formation of the diphosphite ligand from the polymeric precursor of Example 15: Under nitrogen atmosphere, a cold solution (-30° C.) of o-cresol (0.027 g, 0.25 mmol) in toluene (5 mL) was added to a solution of the phosphorochlorodite of phenol (0.045 g, 0.25 mmol) and n-Bu.sub.3N (0.047 g, 0.25 mmol) in toluene (5 mL). The resulting mixture was allowed to stir at room temperature for 1.5 hours, after which it was cooled to -30° C. This cold solution was added to a cold slurry of polymer from example 15 (0.328 g, 0.10 mmol) and n-Bu.sub.3N (0.047 g, 0.25 mmol) in toluene (5 mL). This mixture was stirred at room temperature for five hours. The polymer product was isolated by filtration and washed with toluene and acetonitrile. After drying under vacuum, a tacky solid (0.350 g) was obtained.

DETD [0265] Aspect 10: Semi-batch hydrocyanation of 3-pentenenitrile: To 0.388 g of the catalyst from Example 18B was added 19 mg of zinc chloride and 5 mL of 3PN. The mixture was heated in a 70 C. oil bath and HCN was delivered with 12 cc/min. nitrogen flow rate. After 180 minutes, GC indicated 93.9% conversion to dinitrile with ADN selectivity of 88.4%.

IT 106-99-0, Butadiene, reactions 4635-87-4,
3-Pentenenitrile

(hydrocyanation of; manufacture of unsatd. phosphorus-containing compns.
and
their use in hydrocyanation, isomerization and hydroformylation
reactions)

IT 74-85-1, Ethylene, reactions 74-90-8, Hydrogen cyanide,
reactions 79-97-0, 2,2-Bis(4-hydroxy-3-methylphenyl)propane 814-68-6,
Acryloyl chloride 7719-12-2, Phosphorus trichloride 13185-00-7,
6,6'-Dibromo-2,2'-dihydroxy-1,1'-binaphthyl 26567-10-2 31860-10-3
50291-18-4 100930-72-1 532941-08-5 538345-81-2 538346-27-9
538346-36-0
(manufacture of unsatd. phosphorus-containing compns. and their use in
hydrocyanation, isomerization and hydroformylation reactions)

IT 106-99-0, Butadiene, reactions 4635-87-4,
3-Pentenenitrile
(hydrocyanation of; manufacture of unsatd. phosphorus-containing compns.
and
their use in hydrocyanation, isomerization and hydroformylation
reactions)

RN 106-99-0 USPATFULL
CN 1,3-Butadiene (CA INDEX NAME)



RN 4635-87-4 USPATFULL
CN 3-Pentenenitrile (CA INDEX NAME)



IT 74-90-8, Hydrogen cyanide, reactions
(manufacture of unsatd. phosphorus-containing compns. and their use in
hydrocyanation, isomerization and hydroformylation reactions)

RN 74-90-8 USPATFULL
CN Hydrocyanic acid (CA INDEX NAME)



L88 ANSWER 53 OF 60 USPATFULL on STN
ACCESSION NUMBER: 2003:65616 USPATFULL Full-text
TITLE: Copper-catalyzed vapor phase hydrocyanation of
diolefinic compounds
INVENTOR(S): Douglas Drulner, Joe, Newark, DE, UNITED STATES
Andrew Harmer, Mark, Kennett Square, PA, UNITED STATES
Herron, Norman, Newark, DE, UNITED STATES
Lecloux, Daniel, Wilmington, DE, UNITED STATES

| | NUMBER | KIND | DATE | |
|---------------------|----------------|------|----------|------|
| PATENT INFORMATION: | US 2003045740 | A1 | 20030306 | <-- |
| | US 6753440 | B2 | 20040622 | |
| APPLICATION INFO.: | US 2002-140736 | A1 | 20020508 | (10) |

| | NUMBER | DATE |
|-----------------------|--|---------------|
| PRIORITY INFORMATION: | US 2001-290294P | 20010511 (60) |
| DOCUMENT TYPE: | Utility | |
| FILE SEGMENT: | APPLICATION | |
| LEGAL REPRESENTATIVE: | E I DU PONT DE NEMOURS AND COMPANY, LEGAL PATENT RECORDS CENTER, BARLEY MILL PLAZA 25/1128, 4417 LANCASTER PIKE, WILMINGTON, DE, 19805 | |

NUMBER OF CLAIMS: 18
 EXEMPLARY CLAIM: 1
 LINE COUNT: 496

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB A catalyzed vapor phase process for the hydrocyanation of acyclic diolefinic compounds to olefinic nitriles is described in which the olefinic double bond is not conjugated to the triple bond of the cyano group, wherein a catalyst composition comprising supported copper salts is used.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

TI Copper-catalyzed vapor phase hydrocyanation of diolefinic compounds
 AB A catalyzed vapor phase process for the hydrocyanation of acyclic diolefinic compounds to olefinic nitriles is described in which the olefinic double bond is not conjugated to the triple bond of the cyano group, wherein a catalyst composition comprising supported copper salts is used.
 SUMM . . . the invention relates to a gas phase process for the hydrocyanation of diolefinic compounds to produce nonconjugated acyclic nitriles utilizing catalyst compositions comprising copper salts, dispersed on supports, including carbon, silica, alumina and a variety of metal oxides.

SUMM [0003] Catalytic hydrocyanation systems, particularly pertaining to the hydrocyanation of olefins, are known in the art. For example, liquid phase systems useful. . .

SUMM . . . the liquid phase, with all attendant waste disposal problems. For example, U.S. Pat. No. 4,240,976 utilized copper halide as a catalyst; U.S. Pat. No. 4,230,634 utilized copper inorganic salts in the presence of organic nitriles; and U.K. Patent No. 2,077,260 used. . . further hydrocyanated. For example, U.S. Pat. No. 3,584,029 teaches that propionitrile is prepared by reaction of HCN with ethylene over catalysts containing Ni salts, H_{sub}.3PO_{sub}.4 and Al_{sub}.20.sub.3; and U.S. Pat. No. 3,547,972 discloses the reaction of HCN and butadiene in the gas phase over a mixed metal catalyst containing copper chromite and activated copper chromite, which does yield a mixture of pentenenitriles, with 77-82% selectivities to 3-pentenenitrile and. . .

SUMM [0005] Several patents teach that reaction of HCN with butadiene, ethylene, propylene or butenes, and additionally with air or oxygen in the gas phase, over various supported metal-containing catalysts give rise to cyanated olefinic products. However, in the olefinic products so produced the olefinic double bond is usually conjugated. . .

SUMM [0010] The present invention provides a catalyzed gas phase process for the hydrocyanation of diolefinic compounds which is rapid, selective, and efficient. While certain solvents or diluents can be used in this process, they can be eliminated altogether. Furthermore, the catalyst composition is utilized as a stationary solid phase, which

can reduce the cost of catalyst synthesis, recovery, and recycle, as well as the disposal cost of by-product waste. A corollary benefit is the reduction of . . .

SUMM . . . HCN in the gas phase within a temperature range of 135° C. to 200° C. in the presence of a catalyst composition that is a supported copper (I) or (II) fluorinated alkylsulfonate complex. Preferably the support used in such a catalyst composition is selected from the group consisting of silica, alumina, and carbon; more preferably the support is silica or carbon. Preferably the fluorinated alkylsulfonate in the copper complex in the catalyst composition is trifluoromethylsulfonate.

SUMM . . . HCN in the gas phase within a temperature range of 135° C. to 200° C. in the presence of a catalyst composition that is a copper (I) or (II) complex supported on a fluorosulfonated support. Also preferably the fluorosulfonated support is a composite of a porous silica network within and throughout which is dispersed either a Nafion® perfluorinated polymer or fluorosulfonic acid.

SUMM . . . involves dissolving at least one of HCN and 1,3-butadiene in a solvent, inert to the starting materials and to the catalyst composition under the reaction conditions, prior to being introduced into the reaction, with the solution being vaporized prior to its. . .

SUMM [0015] A catalyst composition useful in the practice of the present invention includes a copper (I) or (II) fluorinated alkylsulfonate complex supported on. . . anions. A preferred support is silica, alumina, carbon and the like. Commonly used techniques for treatment of supports with metal catalysts can be found in B. C. Gates, *Heterogeneous Catalysis*, Vol. 2, pp. 1-29, Ed. B. L. Shapiro, Texas A & M University Press, College Station, Tex., 1984. Typically, in. . . (II) fluorinated alkylsulfonate complex is dispersed on a silica, alumina or carbon support at a concentration sufficient to produce a catalyst composition, including the support, containing 0.3% wt. to 1.0% wt. copper by weight of the total of the composition.

SUMM [0017] Catalyst compositions useful in the practice of the present invention also include copper (I) or (II) complexes supported on a fluorosulfonated. . . R--SO₃.sup.- groups, where R is as defined above or is --C_nF_{2n}--. Preferably the fluorosulfonated support is a composite of a porous silica network within and throughout which is dispersed either a Nafion® perfluorinated polymer or fluorosulfonic acid. Such a composite is. . .

SUMM [0018] In the process of the invention, the catalyst composition is loaded into a tubular reactor, and a gaseous diolefinic compound, e.g., butadiene, and HCN are passed continuously over the solid catalyst composition at a temperature sufficiently high to maintain the starting materials as well as the reaction products in the gas. . . to maintain all of the reactants and products in the gas phase but low enough to prevent deterioration of the catalyst composition. The particular preferred temperature depends to some extent on the catalyst composition being used, the diolefinic compound being used, and the desired reaction rate. The operating pressure is not particularly critical. . .

SUMM . . . a neat vapor or as a preheated solution in a solvent, such as acetonitrile or toluene. Under atmospheric pressure, using nitrogen or another inert gas as a carrier, a temperature of from about 160° C. to 175° C. is typically used. Nitrogen is preferred because of its low cost. Gaseous oxygen, water vapor, or any other gaseous substance which could react with the HCN, the copper portion of the catalyst composition, or the starting diolefinic compound should be avoided. The reaction products are liquid at room temperature and are conveniently. . .

- SUMM . . . in the production of adiponitrile. Other suitable diolefinic compounds include diolefinic compounds substituted with groups which do not deactivate the catalyst composition, for example, cis and trans-1,3-pentadienes.
- SUMM . . . of the present invention, a reactor, such as a tubular reactor, is charged in an inert atmosphere with the desired catalyst composition. The reactor feed and exit lines are preferably purged with an inert gas, such as nitrogen, argon or helium. The reactor is then heated to the desired temperature, either under a continuous flow of inert gas or sealed from. . . the solvent should be gaseous at the reaction temperature and pressure and inert towards the diolefinic compound, HCN, and the catalyst. Such solvents include hydrocarbons such as hexane, benzene, or toluene, or nitriles such as acetonitrile. When the reactants are fed. . .
- SUMM . . . condense all products to liquids. The flow rate of the diolefinic compound preferably is such that its mole ratio to catalyst, per hour of continuous feed, is about 2:1 to 10:1. The mole ratio of the diolefinic compound to HCN normally. . .
- SUMM Preparation of Catalyst Compositions
- SUMM [0027] Copper(I) trifluoromethanesulfonate on Sibunit carbon 7 Inside a nitrogen filled glove box, 0.38 g (1 meq) copper(I) (acetonitrile).sub.4-trifluoromethanesulfonate (prepared according to: Kubas, G. J. Inorg. Synth. 1990, 28, 68-70) was dissolved into 5 mL dry acetonitrile. 1.0 g of 12-20 mesh size Sibunit carbon 7 (Boreskov Inst. of Catalysis, Novosibirsk, Russia), dried previously at 850° C. for 5 hrs in dry helium, was added to the solution and then the slurry was stirred for 15 mins. The solvent was evaporated under vacuum. . . re-wetted with minimal acetonitrile and re-evaporated to help insure complete incorporation of the copper material into the carbon. The recovered catalyst composition was stored under nitrogen until it was loaded into the hydrocyanation reactor for testing.
- SUMM [0029] The procedure to prepare Composition 1 was repeated except substituting 1 g of dry (850° C. in helium for 5 hrs) 20-40 mesh carbon CX0648-1 from EM Science (480 S. Democrat Rd, Gibbstown, N.J. 08027) for the Sibunit. . .
- SUMM [0030] The procedure of example 1 was repeated except substituting 1 g of dry (500° C. in dry air for 1 hr) 10-20 mesh large pore silica-gel granules #89346 from Alfa Aesar (30 Bond Street, Ward Hill, Mass. 01835-8099). . .
- SUMM . . . except substituting 0.25 g copper(I) (acetonitrile).sub.4 hexafluoroantimonate (prepared according to: Kubas, op. cit.) for the trifluoromethane sulfonate salt. The final catalyst was dried in flowing helium at 150° C. for 1 hr then stored under nitrogen.
- SUMM . . . except substituting 0.25 g copper(I) (acetonitrile).sub.4 hexafluorophosphate (prepared according to: Kubas, op. cit.) for the trifluoromethane sulfonate salt. The final catalyst composition was dried in flowing helium at 150° C. for 1 hr then stored under nitrogen.
- SUMM [0037] 1 g of dry (850° C. helium for 5 hrs) EM carbon as described above was slurried into a solution of 0.25 g copper(II) nitrate hydrate dissolved in methanol. The slurry was stirred then evaporated to dryness. The impregnated carbon was then calcined in flowing helium at 300° C. for 1 hr and then cooled to 200° C. The gas flow was switched to hydrogen and held at 200° C. for 1 hr. The material was flushed with nitrogen and cooled and then stored under nitrogen until testing.
- SUMM Copper(I) Exchanged Zeolite Y
- SUMM [0038] 2 g of zeolite NaY (LZY-52 from Aldrich) was dried at 500° C. in flowing air for 4 hrs. This material was slurried

into a solution of 1.0 g copper(I) (acetonitrile)4 trifluoromethanesulfonate in 25 ml dry acetonitrile in a nitrogen filled glove box and stirred for 16 hrs. The solid was filtered off and washed with acetonitrile before drying in flowing nitrogen at 200° C. for 2 hrs. The copper(I) exchanged zeolite catalyst was stored under nitrogen until testing.

DETD [0039] An empty 0.25-inch (0.64 cm) diameter, 15-inch (37.5 cm) long stainless steel tubular reactor was placed in a nitrogen-filled glove box. A plug of glass wool was placed in the bottom end of the reactor, followed by the amount and type of catalyst composition shown in Table 1. A thermocouple was inserted into the top of the reactor. Both ends of the reactor. . . fittings, and the reactor was removed from the glove box and connected to stainless steel reactor feed lines purged with nitrogen. Attached to the outlet side of the reactor was a valve which could be switched to either a waste receiver. . . mm integral diameter, supplied by J&W Scientific, Folsom, Calif. The stationary phase was cyanopropyl (50%) methylpolysiloxane. Feed streams consisted of nitrogen, gaseous butadiene and, typically, an acetonitrile solution containing HCN and also including cyclohexane as an internal GC standard. The combined. . .

DETD . . . Examples 1.about.6. Control E shows complete inactivity for Cu(0) dispersed on carbon, and Control F shows that Cu(AN).sub.4OTf ion-exchanged into zeolite Y is nearly inactive, compared to high activity when dispersed on Sibunit carbon (Table 1, Example 1). Table 2 shows. . .

DETD . . . 100 times the ratio of GC area % (3PN+4PN+2M3BN)/GC area % (all PNs).

TABLE 1

| Gas-Phase Hydrocyanation of Butadiene, Examples 1-6 | | | | | |
|---|----------------------|-------------------|----------------------|-----------------|-------|
| | Catalyst Composition | Catalyst Comp., g | Feed rate, m mole/hr | N.sub.2, Temp., | |
| Elapsed | % HCN | % Select. | (Cu, m eq.) | BD. | . . . |
| Example (Support) | | | | | |
| DETD [0042] | | | | | |

TABLE 2

Gas-Phase Hydrocyanation of Butadiene, Controls A-F

| | Catalyst Composition | Catalyst Comp., g | Feed rate, milli mole/hr | N.sub.2, Temp., |
|--|----------------------|-------------------|--------------------------|----------------------|
| Elapsed | % HCN | % Select. | (Cu, m eq.) | BD HCN cc/min °. . . |
| Example (Support) | | | | |
| . 3.5 " (EM Carbon) | 0 [0.71] | | | 185 5.8 |
| " | | | | 100 8.8 |
| F Cu(AN).sub.4OTf trace " (Zeolite Y) | 1.05 [0.9] | 4.0 2.5 | " | 165 1.1 2.2 |

CLM What is claimed is:

- . . compounds, comprising reacting an acyclic, aliphatic, conjugated diolefinic compound with HCN in the gas phase in the presence of a catalyst composition comprising either: (a) a supported copper (I) or (II) fluorinated alkylsulfonate complex; or (b) a copper (I) or (II). . .

- . . . of claim 1 wherein the diolefinic compound is substituted with at least one other group which does not deactivate the catalyst composition.
- . . . at least one of HCN and 1,3-butadiene is dissolved in a solvent, inert to the starting materials and to the catalyst composition under the reaction conditions, prior to being introduced into the reaction, but the solution is vaporized prior to its. . .
- . . process of claim 11 wherein the flow rate of the diolefinic compound is such that its mole ratio to the catalyst composition, per hour of continuous feed, is between about 5:1 and about 100:1.

15. The process of claim 1 wherein the catalyst composition comprises Composition (a), a supported copper (I) or (II) fluorinated alkylsulfonate complex.

17. The process of claim 1 wherein the catalyst composition comprises Composition (b), a copper (I) or (II) complex supported on a fluorosulfonated support.

18. The process of claim 17 wherein the fluorosulfonated support is a composite of a porous silica network within and throughout which is dispersed either a perfluorinated polymer or fluorosulfonic acid.

| | | |
|------|---|---|
| IT | 592-51-8P, 4-Pentenenitrile | 1647-11-6P, 2-Cyano-1-butene |
| | 4635-87-4P, 3-Pentenenitrile | (copper-catalyzed vapor-phase hydrocyanation process for the conversion of diolefinic compds. with hydrogen cyanide into unsatd. nitriles) |
| IT | 74-90-8, Hydrogen cyanide, reactions | 106-99-0, Butadiene, reactions (copper-catalyzed vapor-phase hydrocyanation process for the conversion of diolefinic compds. with hydrogen cyanide into unsatd. nitriles) |
| TI | | Copper-catalyzed vapor phase hydrocyanation of diolefinic compounds! |
| PI | US 2003045740 | A1 20030306 |
| | US 6753440 | B2 200406221 |
| AB | | <-- |
| SUMM | A catalyzed vapor phase process for the hydrocyanation of acyclic diolefinic compounds to olefinic nitriles is described in which the olefinic double bond is not conjugated to the triple bond of the cyano group, wherein a catalyst composition comprising supported copper salts is used. [0002] This invention generally relates to a gas phase process for the hydrocyanation of diolefinic compounds to produce nonconjugated acyclic nitriles. In particular, the invention relates to a gas phase process for the hydrocyanation of diolefinic compounds to produce nonconjugated acyclic nitriles utilizing catalyst compositions comprising copper salts, dispersed on supports, including carbon, silica, alumina and a variety of metal oxides. | |
| SUMM | [0003] Catalytic hydrocyanation systems, particularly pertaining to the hydrocyanation of olefins, are known in the art. For example, liquid phase systems useful for the hydrocyanation of butadiene to form pentenenitriles (PNs) are known in the art, e.g., U.S. Pat. No. 3,766,237. As used in that patent and as will be used herein, the term "pentenenitrile" is intended to mean a cyanobutene. Likewise, "butenenitrile" means cyanopropene. The pentenenitriles so formed are further subjected to hydrocyanation and, in some cases isomerization, to form adiponitrile (ADN), a commercially important material in the manufacture of nylon. | |
| SUMM | [0004] The overwhelming majority of prior art processes for the hydrocyanation of butadiene are conducted in the liquid phase, with all | |

attendant waste disposal problems. For example, U.S. Pat. No. 4,240,976 utilized copper halide as a catalyst; U.S. Pat. No. 4,230,634 utilized copper inorganic salts in the presence of organic nitriles; and U.K. Patent No. 2,077,260 used copper bonded to a peroxy group. Previous approaches toward carrying out gas phase hydrocyanation of olefinic compounds have usually started with monoolefinic, not diolefinic, compounds and have given rise primarily to saturated products, which could not be further hydrocyanated. For example, U.S. Pat. No. 3,584,029 teaches that propionitrile is prepared by reaction of HCN with ethylene over catalysts containing Ni salts, H_{sub}.3PO_{sub}.4 and Al_{sub}.20_{sub}.3; and U.S. Pat. No. 3,547,972 discloses the reaction of HCN and butadiene in the gas phase over a mixed metal catalyst containing copper chromite and activated copper chromite, which does yield a mixture of pentenenitriles, with 77-82% selectivities to 3-pentenenitrile and 4-pentenenitrile. However, the reaction of U.S. Pat. No. 3,547,972 also requires a co-feed of HCl.

SUMM [0005] Several patents teach that reaction of HCN with butadiene, ethylene, propylene or butenes, and additionally with air or oxygen in the gas phase, over various supported metal-containing catalysts give rise to cyanated olefinic products. However, in the olefinic products so produced the olefinic double bond is usually conjugated with the triple bond of the cyano group, and, therefore, substantially useless for the production of adiponitrile. For example, see:

SUMM [0010] The present invention provides a catalyzed gas phase process for the hydrocyanation of diolefinic compounds which is rapid, selective, and efficient. While certain solvents or diluents can be used in this process, they can be eliminated altogether. Furthermore, the catalyst composition is utilized as a stationary solid phase, which can reduce the cost of catalyst synthesis, recovery, and recycle, as well as the disposal cost of by-product waste. A corollary benefit is the reduction of the cost of capital equipment needed for the process.

SUMM [0011] One embodiment of the invention is a process for the gas-phase hydrocyanation of diolefinic compounds comprising reacting an acyclic, aliphatic, conjugated diolefinic compound with HCN in the gas phase within a temperature range of 135° C. to 200° C. in the presence of a catalyst composition that is a supported copper (I) or (II) fluorinated alkylsulfonate complex. Preferably the support used in such a catalyst composition is selected from the group consisting of silica, alumina, and carbon; more preferably the support is silica or carbon. Preferably the fluorinated alkylsulfonate in the copper complex in the catalyst composition is trifluoromethylsulfonate.

SUMM [0012] Another embodiment of the invention is a process for the gas-phase hydrocyanation of diolefinic compounds comprising reacting an acyclic, aliphatic, conjugated diolefinic compound with HCN in the gas phase within a temperature range of 135° C. to 200° C. in the presence of a catalyst composition that is a copper (I) or (II) complex supported on a fluorosulfonated support. Also preferably the fluorosulfonated support is a composite of a porous silica network within and throughout which is dispersed either a Nafion® perfluorinated polymer or fluorosulfonic acid.

SUMM [0014] A further embodiment of the invention involves the introduction of HCN and 1,3-butadiene into the reaction without a solvent or diluent. Yet a further embodiment involves dissolving at least one of HCN and 1,3-butadiene in a solvent, inert to the starting materials and to the catalyst composition under the reaction conditions, prior to being

introduced into the reaction, with the solution being vaporized prior to its entry into the reaction.

- SUMM [0015] A catalyst composition useful in the practice of the present invention includes a copper (I) or (II) fluorinated alkylsulfonate complex supported on a carrier that is neutral and has a low surface area. A complex is one or more metal cations together with its associated anions. A preferred support is silica, alumina, carbon and the like. Commonly used techniques for treatment of supports with metal catalysts can be found in B. C. Gates, *Heterogeneous Catalysis*, Vol. 2, pp. 1-29, Ed. B. L. Shapiro, Texas A & M University Press, College Station, Tex., 1984. Typically, in accordance with this invention, the copper (I) or (II) fluorinated alkylsulfonate complex is dispersed on a silica, alumina or carbon support at a concentration sufficient to produce a catalyst composition, including the support, containing 0.3% wt. to 1.0% wt. copper by weight of the total of the composition.
- SUMM [0017] Catalyst compositions useful in the practice of the present invention also include copper (I) or (II) complexes supported on a fluorosulfonated support. A fluorosulfonated support contains R--SO₃.sub.2.sup.- groups, where R is as defined above or is --C_nF_{2n+2}--. Preferably the fluorosulfonated support is a composite of a porous silica network within and throughout which is dispersed either a Nafion® perfluorinated polymer or fluorosulfonic acid. Such a composite is more particularly described in U.S. Pat. Nos. 5,824,622, 5,916,837 and 5,948,946.
- SUMM [0018] In the process of the invention, the catalyst composition is loaded into a tubular reactor, and a gaseous diolefinic compound, e.g., butadiene, and HCN are passed continuously over the solid catalyst composition at a temperature sufficiently high to maintain the starting materials as well as the reaction products in the gas phase. The preferred temperature range is from about 135° C. to about 200° C., most preferably from about 155° C. to about 175° C. The temperature must be high enough to maintain all of the reactants and products in the gas phase but low enough to prevent deterioration of the catalyst composition. The particular preferred temperature depends to some extent on the catalyst composition being used, the diolefinic compound being used, and the desired reaction rate. The operating pressure is not particularly critical and can conveniently be from about 1-10 atmospheres (about 101.3 to about 1013 kPa). No practical benefit is obtained when operating above the upper limit of this pressure range.
- SUMM [0019] HCN and/or diolefinic compound starting materials can be delivered as a neat vapor or as a preheated solution in a solvent, such as acetonitrile or toluene. Under atmospheric pressure, using nitrogen or another inert gas as a carrier, a temperature of from about 160° C. to 175° C. is typically used. Nitrogen is preferred because of its low cost. Gaseous oxygen, water vapor, or any other gaseous substance which could react with the HCN, the copper portion of the catalyst composition, or the starting diolefinic compound should be avoided. The reaction products are liquid at room temperature and are conveniently recovered by cooling. Branched 2-methyl-3-butenenitrile can be separated from linear 3-pentenenitrile and 4-pentenenitrile by distillation.
- SUMM [0020] The diolefinic compound reactants used in this invention include primarily conjugated diolefins containing from 4 to 10 carbon atoms; for

example 1,3-butadiene and cis and trans-2,4-hexadienes. Butadiene is especially preferred by reason of its commercial importance in the production of adiponitrile. Other suitable diolefinic compounds include diolefinic compounds substituted with groups which do not deactivate the catalyst composition, for example, cis and trans-1,3-pentadienes.

SUMM [0024] In the practice of the hydrocyanation process of the present invention, a reactor, such as a tubular reactor, is charged in an inert atmosphere with the desired catalyst composition. The reactor feed and exit lines are preferably purged with an inert gas, such as nitrogen, argon or helium. The reactor is then heated to the desired temperature, either under a continuous flow of inert gas or sealed from the ambient atmosphere. The reactor is fed with the desired diolefinic compound and HCN. These may be fed together or separately, either neat or as solutions in suitable solvents, such as acetonitrile or toluene. The hydrocyanation reaction is, however, preferably carried out without a solvent. If any solvent is used, the solvent should be gaseous at the reaction temperature and pressure and inert towards the diolefinic compound, HCN, and the catalyst. Such solvents include hydrocarbons such as hexane, benzene, or toluene, or nitriles such as acetonitrile. When the reactants are fed continuously, an inert gas carrier normally is employed as well.

SUMM [0025] The diolefinic compound, HCN and any solvent are passed through a heated portion of feed line heated to the reaction temperature to ensure complete vaporization. The gaseous product mixture exiting the reactor can be passed, if desired, through a heated gas sampling loop of a gas chromatograph for periodically monitoring the progress of the reaction. Alternatively, the gaseous effluent can be cooled to about 0°C. to 25°C. in order to condense all products to liquids. The flow rate of the diolefinic compound preferably is such that its mole ratio to catalyst, per hour of continuous feed, is about 2:1 to 10:1. The mole ratio of the diolefinic compound to HCN normally is at least about 1:1.

SUMM Preparation of Catalyst Compositions

SUMM [0027] Copper(I) trifluoromethanesulfonate on Sibunit carbon 7 Inside a nitrogen filled glove box, 0.38 g (1 meq) copper(I) (acetonitrile).sub.4-trifluoromethanesulfonate (prepared according to: Kubas, G. J. Inorg. Synth. 1990, 28, 68-70) was dissolved into 5 mL dry acetonitrile. 1.0 g of 12-20 mesh size Sibunit carbon 7 (Boreksov Inst. of Catalysis, Novosibirsk, Russia), dried previously at 850°C. for 5 hrs in dry helium, was added to the solution and then the slurry was stirred for 15 mins. The solvent was evaporated under vacuum and the resulting solid was re-wetted with minimal acetonitrile and re-evaporated to help insure complete incorporation of the copper material into the carbon. The recovered catalyst composition was stored under nitrogen until it was loaded into the hydrocyanation reactor for testing.

SUMM [0029] The procedure to prepare Composition 1 was repeated except substituting 1 g of dry (850°C. in helium for 5 hrs) 20-40 mesh carbon CX0648-1 from EM Science (480 S. Democrat Rd, Gibbstown, N.J. 08027) for the Sibunit 7 carbon.

SUMM [0030] The procedure of example 1 was repeated except substituting 1 g of dry (500°C. in dry air for 1 hr) 10-20 mesh large pore silica-gel granules #89346 from Alfa Aesar (30 Bond Street, Ward Hill,

Mass. 01835-8099) for the Sibunit 7 carbon.

- SUMM [0034] The procedure to prepare Composition 3 was repeated except substituting 0.25 g copper(I) (acetonitrile).sub.4 hexafluoroantimonate (prepared according to: Kubas, op. cit.) for the trifluoromethane sulfonate salt. The final catalyst was dried in flowing helium at 150° C. for 1 hr then stored under nitrogen.
- SUMM [0035] The procedure to prepare Composition 3 was repeated except substituting 0.25 g copper(I) (acetonitrile).sub.4 hexafluorophosphate (prepared according to: Kubas, op. cit.) for the trifluoromethane sulfonate salt. The final catalyst composition was dried in flowing helium at 150° C. for 1 hr then stored under nitrogen.
- SUMM [0037] 1 g of dry (850° C. helium for 5 hrs) EM carbon as described above was slurried into a solution of 0.25 g copper(II) nitrate hydrate dissolved in methanol. The slurry was stirred then evaporated to dryness. The impregnated carbon was then calcined in flowing helium at 300° C. for 1 hr and then cooled to 200° C. The gas flow was switched to hydrogen and held at 200° C. for 1 hr. The material was flushed with nitrogen and cooled and then stored under nitrogen until testing.
- SUMM Copper(I) Exchanged Zeolite Y
- SUMM [0038] 2 g of zeolite NaY (LZY-52 from Aldrich) was dried at 500° C. in flowing air for 4 hrs. This material was slurried into a solution of 1.0 g copper(I) (acetonitrile)4 trifluoromethanesulfonate in 25 mL dry acetonitrile in a nitrogen filled glove box and stirred for 16 hrs. The solid was filtered off and washed with acetonitrile before drying in flowing nitrogen at 200° C. for 2 hrs. The copper(I) exchanged zeolite catalyst was stored under nitrogen until testing.
- DETD [0039] An empty 0.25-inch (0.64 cm) diameter, 15-inch (37.5 cm) long stainless steel tubular reactor was placed in a nitrogen-filled glove box. A plug of glass wool was placed in the bottom end of the reactor, followed by the amount and type of catalyst composition shown in Table 1. A thermocouple was inserted into the top of the reactor. Both ends of the reactor were sealed with metal fittings, and the reactor was removed from the glove box and connected to stainless steel reactor feed lines purged with nitrogen. Attached to the outlet side of the reactor was a valve which could be switched to either a waste receiver or a heated tubing line for diverting the gaseous effluent to an injector for analysis by gas chromatography (GC). GC analyses were done on a 30 m DB-23 capillary column of a 0.32 mm integral diameter, supplied by J&W Scientific, Folsom, Calif. The stationary phase was cyanopropyl (50%) methylpolysiloxane. Feed streams consisted of nitrogen, gaseous butadiene and, typically, an acetonitrile solution containing HCN and also including cyclohexane as an internal GC standard. The combined feed streams were preheated to 150° C. to ensure complete vaporization. The reactor was heated in a split tube furnace to the temperatures shown in Table 1. Product samples were collected, generally every hour. Table 1 shows the specific reaction conditions and summarizes the results.
- DETD [0040] Controls A.about.F show comparative versions of the hydrocyanation of butadiene using several Cu(I) salts dispersed on carbon which are either inactive or exhibit short-lived low activity. Controls A.about.F were run under a process comparable to that of

Examples 1.about.6. Control E shows complete inactivity for Cu(0) dispersed on carbon, and Control F shows that Cu(AN).sub.4OTf ion-exchanged into zeolite Y is nearly inactive, compared to high activity when dispersed on Sibunit carbon (Table 1, Example 1). Table 2 shows the specific reaction conditions and summarizes the results.

DETDS [0041] Percent conversion of HCN was calculated as (measured GC area % for PNs/measured GC area % for cyclohexane)×(GC response factor for PNs)×(mmoles of cyclohexane fed per hour/mmole of HCN fed per hour)×100. Response factor is the number, characteristic for each compound, required for converting area percent to mole percent of PNs. Percent Linear was determined as 100 times the ratio of GC area % $(3PN+4PN)/GC\ area\ %$ $(3PN+4PN+2M3BN)$. Percent selectivity to useful PNs $(3PN+4PN+2M3BN)$ was determined as 100 times the ratio of GC area % $(3PN+4PN+2M3BN)/GC\ area\ %$ (all PNs).

TABLE 1

Gas-Phase Hydrocyanation of Butadiene, Examples 1-6

| Example | (Support) | Catalyst | Catalyst | Feed rate, | | N.sub.2, Temp., | | |
|------------------|------------------|-------------|-------------|------------|-----------|-----------------|------|-----|
| | | Composition | Comp., g | m mole/hr | % Select. | | | |
| Elapsed time, hr | % Linear | % HCN Conv. | (Cu, m eq.) | BD | HCN | cc/min | ° C. | |
| 1 | Cu(AN).sub.4OTf | 1.03 | | 2.1 | 1.1 | 5 | 175 | 1.1 |
| | 88.9 | 56.2 | 100 | | | | | 3.2 |
| | (Sibunit Carbon) | | (1.0) | | | | | |
| | 88.2 | 81.6 | " | | | | | |
| 5.2 | 91.1 | 99.5 | " | | | | | |
| 7.2 | 92.8 | 78.4 | " | | | | | |
| 9.3 | 91.9 | 64.5 | " | | | | | |
| 11.3 | 89.2 | 54.1 | " | | | | | |
| 13.3 | 90.0 | 51.4 | " | | | | | |
| 15.4 | 91.7 | 39.5 | " | | | | | |
| 2 | Cu(OTf).sub.2 | 1.6 | | 2.1 | 1.1 | 5 | 175 | 2 |
| | 84.2 | 48.5 | 100 | | | | | 3 |
| | (Sibunit Carbon) | | (1.0) | | | | | |
| | 84.0 | 40.9 | " | | | | | 5 |
| | 86.7 | 49.8 | " | | | | | |
| 7 | 91.2 | 69.7 | " | | | | | |
| 9.1 | 90.8 | 89.6 | " | | | | | |
| 11.1 | 90.5 | 81.7 | " | | | | | |
| 13.1 | 90.9 | 66.5 | " | | | | | |
| 15.1 | 89.0 | 58.5 | " | | | | | |
| 3 | Cu(AN).sub.4OTf | 1.48 | | 4.0 | 2.9 | 0 | 160 | 1.5 |
| | 88.2 | 24.5 | 100 | | | | | 2.8 |
| | (EM Carbon) | | (1.0) | | | | | |
| | 90.3 | 33.3 | " | | | | | |
| 3.8 | 90.0 | 20.1 | " | | | | | |
| 4.8 | 90.0 | 11.6 | " | | | | | |
| 22.3 | | 0.9 | " | | | | | |
| 4 | Cu(AN).sub.4OTf | 1.33 | | 2.1 | 1.2 | 5 | 175 | 1 |
| | 88.5 | 41.4 | 100 | | | | | 2.5 |
| | (Silica) | | (1.0) | | | | | |
| | 88.8 | 83.9 | " | | | | | |
| 6.5 | 89.0 | 65.8 | " | | | | | |
| 12.5 | 87.9 | 50.0 | " | | | | | |
| 17.5 | 88.8 | 38.1 | " | | | | | |

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| | | | | | | | | |
|------|-------------------|-------|---|-----|-----|---|-----|-----|
| 21.5 | 93.2 | 33.4 | " | | | | | |
| 5 | Cu(AN).sub.4OTf | 1.19 | | 2.1 | 1.2 | 5 | 175 | 1 |
| 87.8 | 78.9 | 100 | | | | | | |
| | (Nafion ®/Silica) | (1.0) | | | | | | |
| 2.5 | 90.2 | 97.1 | " | | | | | |
| 5.1 | 90.1 | 88.8 | " | | | | | |
| 9.1 | 87.1 | 96.5 | " | | | | | |
| 16.1 | 90.2 | 72.6 | " | | | | | |
| 20.1 | 89.2 | 52.7 | " | | | | | |
| 24.5 | 89.3 | 34.1 | " | | | | | |
| 6 | Cu(AN).sub.4OTf | 1.63 | | 2.1 | 1.2 | 5 | 175 | 0.5 |
| 45.5 | 14 | 100 | | | | | | |
| | (derivatized | [] | | | | | | 3.5 |
| 86.2 | 105.4 | " | | | | | | 6.5 |
| | Silica) | | | | | | | |
| 91.5 | 98.7 | " | | | | | | |
| 12.5 | 90.6 | 88.9 | " | | | | | |
| 19.5 | 90.3 | 78.4 | " | | | | | |
| 24.5 | 88.4 | 56.3 | " | | | | | |
| DETD | [0042] | | | | | | | |

TABLE 2

Gas-Phase Hydrocyanation of Butadiene, Controls A-F

| Example | Elapsed time, hr | Catalyst Composition (Support) | % Linear | Feed rate, | | | | | |
|---------|------------------|-----------------------------------|----------|-------------------|---------------|-------------------|-----------|-----|-----|
| | | | | Catalyst Comp., % | milli mole/hr | N.sub.2, Temp., | | | |
| | | | | | | % HCN (Cu, m eq.) | % Select. | | |
| A | | Cu(tosylate) | 1.36 | | 4.0 | 2.9 | 0 | 160 | 1 |
| | 2.0 | 100 | | | | | | | |
| | | (EM Carbon) | (1.0) | | | | | | 2 |
| | 3.3 | " | | | | | | | |
| 4 | | | 1.4 | " | | | | | |
| 5 | | | 1.0 | " | | | | | |
| B | | Cu(AN).sub.4SbF.sub.6 | 0.62 | | 5.4 | 2.6 | " | 165 | 1 |
| | trace | | | | | | | | |
| | | (EM Carbon) | [0.27] | | " | 1.3 | " | " | 3 |
| | " | | | | | | | | |
| | | | | | | | | | |
| C | 0 | Cu(AN).sub.4PF.sub.6 | 0.5 | | 5.4 | 1.0 | " | 165 | 1 |
| 0 | | | | | | | | | |
| | | (EM Carbon) | [0.27] | | | | | | 3 |
| | " | | | | | | | | |
| D | 5 | | " | | | | | | |
| | 1.8 | CuCl | 1.14 | | 4.0 | 2.9 | " | 160 | 2.2 |
| | 1.3 | (EM Carbon) | (1.0) | | | | | " | 3.3 |
| | 0.6 | | | | | | | 180 | 5.1 |
| | 0.3 | | | | | | | " | 6.2 |
| E | 0 | Cu(O) | 0.58 | | 5.4 | 2.6 | " | 165 | 3.5 |
| | " | (EM Carbon) | [0.71] | | | | | 185 | 5.8 |

| | | | | | | |
|-------|--|------------------------------|-----|-----|-----|-----|
| | | | | | 100 | 8.8 |
| " | | | | | | |
| F | Cu(AN).sub.4OTf | 1.05 | 4.0 | 2.5 | " | 165 |
| trace | (Zeolite Y) | [0.9] | | | | 2.2 |
| 0 | | | | | | |
| 1. | A process for the gas-phase hydrocyanation of diolefinic compounds, comprising reacting an acyclic, aliphatic, conjugated diolefinic compound with HCN in the gas phase in the presence of a catalyst composition comprising either: (a) a supported copper (I) or (II) fluorinated alkylsulfonate complex; or (b) a copper (I) or (II) complex supported on a fluorosulfonated support. | | | | | |
| 7. | The process of claim 1 wherein the diolefinic compound is substituted with at least one other group which does not deactivate the catalyst composition. | | | | | |
| 9. | The process of claim 7 wherein at least one of HCN and 1,3-butadiene is dissolved in a solvent, inert to the starting materials and to the catalyst composition under the reaction conditions, prior to being introduced into the reaction, but the solution is vaporized prior to its entry into the reaction. | | | | | |
| 12. | The process of claim 11 wherein the flow rate of the diolefinic compound is such that its mole ratio to the catalyst composition, per hour of continuous feed, is between about 5:1 and about 100:1. | | | | | |
| 15. | The process of claim 1 wherein the catalyst composition comprises Composition (a), a supported copper (I) or (II) fluorinated alkylsulfonate complex. | | | | | |
| 17. | The process of claim 1 wherein the catalyst composition comprises Composition (b), a copper (I) or (II) complex supported on a fluorosulfonated support. | | | | | |
| 18. | The process of claim 17 wherein the fluorosulfonated support is a composite of a porous silica network within and throughout which is dispersed either a perfluorinated polymer or fluorosulfonic acid. | | | | | |
| IT | 592-51-8P, 4-Pentenenitrile | 1647-11-6P, 2-Cyano-1-butene | | | | |
| | 4635-87-4P, 3-Pentenenitrile | | | | | |
| | (copper-catalyzed vapor-phase hydrocyanation process for the conversion of diolefinic compds. with hydrogen cyanide into unsatd. nitriles) | | | | | |
| IT | 74-90-8, Hydrogen cyanide, reactions 106-99-0, | | | | | |
| | Butadiene, reactions | | | | | |
| | (copper-catalyzed vapor-phase hydrocyanation process for the conversion of diolefinic compds. with hydrogen cyanide into unsatd. nitriles) | | | | | |
| IT | 4635-87-4P, 3-Pentenenitrile | | | | | |
| | (copper-catalyzed vapor-phase hydrocyanation process for the conversion of diolefinic compds. with hydrogen cyanide into unsatd. nitriles) | | | | | |
| RN | 4635-87-4 USPATFULL | | | | | |
| CN | 3-Pentenenitrile (CA INDEX NAME) | | | | | |



IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,

Butadiene, reactions

(copper-catalyzed vapor-phase hydrocyanation process for the conversion
of diolefinic compds. with hydrogen cyanide into unsatd. nitriles)

RN 74-90-8 USPATFULL

CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 USPATFULL

CN 1,3-Butadiene (CA INDEX NAME)



L88 ANSWER 54 OF 60 USPATFULL on STN

ACCESSION NUMBER: 2003:47857 USPATFULL Full-text

TITLE: Catalyst comprising a complex of a metal from subgroup VIII based on a bidentate phosphonite ligand, and method for producing nitriles

INVENTOR(S): Fischer, Jakob, Kirchdorf, GERMANY, FEDERAL REPUBLIC OF Siegel, Wolfgang, Limburgerhof, GERMANY, FEDERAL REPUBLIC OF Keitel, Dagmar Pascale, Limburgerhof, GERMANY, FEDERAL REPUBLIC OF Siggel, Lorenz, Heidelberg, GERMANY, FEDERAL REPUBLIC OF

PATENT ASSIGNEE(S): BASF Aktiengesellschaft, Ludwigshafen, GERMANY, FEDERAL REPUBLIC OF (non-U.S. corporation)

| | NUMBER | KIND | DATE | |
|---------------------|----------------|------|--------------|-----|
| PATENT INFORMATION: | US 6521778 | B1 | 20030218 | <-- |
| | WO 9964155 | | 19991216 | |
| APPLICATION INFO.: | US 2000-701601 | | 20001130 (9) | |
| | WO 1999-EP3888 | | 19990604 | |

| | NUMBER | DATE |
|-----------------------|--|----------|
| PRIORITY INFORMATION: | DE 1998-19825212 | 19980605 |
| DOCUMENT TYPE: | Utility | |
| FILE SEGMENT: | GRANTED | |
| PRIMARY EXAMINER: | McKane, Joseph K. | |
| ASSISTANT EXAMINER: | Anderson, Rebecca | |
| LEGAL REPRESENTATIVE: | Keil & Weinkauf | |
| NUMBER OF CLAIMS: | 14 | |
| EXEMPLARY CLAIM: | 1 | |
| NUMBER OF DRAWINGS: | 0 Drawing Figure(s); 0 Drawing Page(s) | |
| LINE COUNT: | 934 | |

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB A catalyst which comprises at least one complex of a metal of subgroup VIII having at least one bidentate phosphonite ligand of the formula I ##STR1##

or salts and mixtures thereof, a process for the preparation of mixtures of monoolefinic C.sub.5-mononitriles, a process for the catalytic isomerization of branched aliphatic monoalkenenitriles and a process for the preparation of adiponitrile.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

- TI Catalyst comprising a complex of a metal from subgroup VIII based on a bidentate phosphonite ligand, and method for producing nitriles
- AB A catalyst which comprises at least one complex of a metal of subgroup VIII having at least one bidentate phosphonite ligand of. . .
- AB or salts and mixtures thereof, a process for the preparation of mixtures of monoolefinic C.sub.5-mononitriles, a process for the catalytic isomerization of branched aliphatic monoalkenenitriles and a process for the preparation of adiponitrile.
- SUMM The present invention relates to a catalyst which comprises a complex of a metal of subgroup VIII, which comprises at least one bidentate phosphonite ligand, a process for the preparation of mixtures of monoolefinic C.sub.5-mononitriles and a process for the preparation of adiponitrile by catalytic hydrocyanation in the presence of such a catalyst.
- SUMM "Applied Homogeneous Catalysis with Organometallic Compounds", Vol. 1, VCH Weinheim, page 465 et seq., describes in general the addition reaction of hydrogen cyanide with olefins under heterogeneous and homogeneous catalysis. In particular, catalysts based on phosphine, phosphite and phosphonite complexes of nickel and of palladium are used. For the preparation of adiponitrile by hydrocyanation of butadiene, predominantly nickel(0) phosphite catalysts are used, in the presence or absence of a Lewis acid as a promoter.
- SUMM J. Chem. Soc., Chem. Commun., 1991, page 1292, describes chiral aryl diphosphites as ligands for hydrocyanation catalysts. In these ligands, the phosphite group is bonded via two of its oxygen atoms to the 3- and 3'-positions of. . .
- SUMM U.S. Pat. No. 5,449,807 describes a process for the gas-phase hydrocyanation of diolefins in the presence of a supported nickel catalyst based on at least one bidentate phosphite ligand, the two phosphite groups being bridged by an unsubstituted or substituted 2,2'-biphenyl. . . describes a process for the gas-phase isomerization of 2-alkyl-3-monoalkenenitriles to give linear 3- and/or 4-monoalkenenitriles in the presence of the catalysts described in U.S. Pat. No. 5,449,807.
- SUMM WO 95/14659 describes a process for the hydrocyanation of monoolefins, in which catalysts based on zero-valent nickel and bidentate phosphite ligands may be used. In these ligands, the phosphite groups together with two. . .
- SUMM U.S. Pat. No. 5,512,695 likewise describes a process for the hydrocyanation of monoolefins in the presence of a nickel catalyst which comprises a bidentate phosphite ligand.
- SUMM WO 96/11182 describes a process for hydrocyanation in the presence of a nickel catalyst based on a bidentate or polydentate phosphite ligand in which the phosphite groups are not part of a heterocycle. The. . .
- SUMM U.S. Pat. No. 5,523,453 describes a process for hydrocyanation in the presence of a nickel catalyst based on a bidentate ligand which comprises at least one phosphinite group and a further phosphorus-containing group which is selected. . . WO 97/23446 describes a process for the hydrocyanation of diolefins and for the isomerization of 2-alkyl-3-monoalkenenitriles in the presence of catalysts which correspond to those described in U.S. Pat. No.

- 5,523,453.
- SUMM . . . describes a process for the hydrocyanation of diolefinic compounds and for the isomerization of the resulting, nonconjugated 2-alkyl-3-monoalkenenitriles, a nickel(0) catalyst based on a polydentate phosphite ligand being used in the presence of a Lewis acid as promoter. The phosphite groups. . .
- SUMM None of the abovementioned publications describes hydrocyanation catalysts based on phosphonite ligands. In particular, no catalysts based on bidentate chelate phosphonites are described.
- SUMM . . . hydrocyanation of ethylenically unsaturated compounds which may have further functional groups, such as nitriles, in the presence of a nickel catalyst. These nickel catalysts carry four ligands of the formula M(X,Y,Z), where X, Y and Z, independently of one another, are each a radical. . . the hydrocyanation. On the other hand, it is not disclosed that phosphonites can be used as ligands for nickel(0) hydrocyanation catalysts. In particular, no bidentate chelate phosphonite ligands are described.
- SUMM It is an object of the present invention to provide novel catalysts based on a metal of subgroup VIII. They should preferably have good selectivity and good catalytic activity in the hydrocyanation of 1,3-butadiene and 1,3-butadiene-containing hydrocarbon mixtures. Preferably, they should also be suitable for the catalytic isomerization of monoalkenenitriles and for the addition reaction of the second molecule of hydrogen cyanide with said monoalkenenitriles, for example. . .
- SUMM We have surprisingly found that this object is achieved by catalysts based on a metal of subgroup VIII which comprise at least one bidentate phosphonite ligand.
- SUMM The present invention therefore relates to a catalyst comprising a complex of a metal of subgroup VIII, having a bidentate phosphonite ligand of the formula I ##STR2##
- SUMM The novel catalysts may have one or more of the phosphonite ligands of the formula I. In addition to the ligands of formula. . .
- SUMM Preferably, the metal of subgroup VIII is cobalt, rhodium, ruthenium, palladium or nickel. If the novel catalysts are used for hydrocyanation, the metal of subgroup VIII is in particular nickel.
- SUMM For the preparation of the phosphonite ligands of the formula I which are used in the novel catalysts, a dihalophosphorus(III) compound III, where R.sup.1 (or R.sup.1') has the abovementioned meanings, can first be reacted with a monoalcohol IV, . . .
- SUMM For the preparation of the novel catalysts, at least one phosphonite ligand of the formula I can be reacted with a metal of subgroup VIII, e.g. nickel, . . .
- SUMM . . . haloalkanes, for example dichloromethane, chloroform, dichloroethane and trichloroethane. Other suitable solvents are the liquid starting materials and/or products of the catalyzed reaction. The temperature is from -70 to 150° C., preferably from 0° C. to 100° C., particularly preferably about room. . .
- SUMM . . . the form of a powder. The reaction of nickel and phosphonite ligand is preferably effected in a product of the catalyzed reaction, such as the hydrocyanation reaction, as the solvent, for example in a mixture of monoolefinic C.sub.5-mononitriles or, preferably, in. . .
- SUMM . . . relates to a process for the preparation of mixtures of monoolefinic C.sub.5-mononitriles having a nonconjugated C.dbd.C and C.tbd.N bond by catalytic hydrocyanation of butadiene or of a 1,3-butadiene-containing hydrocarbon mixture, wherein the hydrocyanation is carried out in the presence of at least one of the novel catalysts described above.
- SUMM . . . be obtained in which a C.dbd.C double bond is present in conjugation with the C.tbd.N bond. These may act as catalyst poisons

for the first reaction step of the adipic acid preparation, the monoaddition reaction of hydrogen cyanide.

SUMM If required, those components which may give rise to catalyst poisons, in particular alkynes, 1,2-dienes and mixtures thereof, are therefore partially or completely removed from the hydrocarbon mixture. To remove these components, the C.sub.4 cut is subjected to a partial catalytic hydrogenation before the addition reaction with hydrogen cyanide. This partial hydrogenation is effected in the presence of a hydrogenation catalyst which is capable of hydrogenating alkynes and 1,2-dienes selectively alongside other dienes and monoolefins.

SUMM Suitable heterogeneous catalyst systems for the selective hydrogenation are known and comprise in general a transition metal compound on an inert support. They . . . particular those described in U.S. Pat. Nos. 4,587,369, 4,704,492 and 4,493,906, which are hereby fully incorporated by reference. Further suitable catalyst systems based on copper are sold by Dow Chemical as KLP catalyst.

SUMM . . . der technischen Chemie, Vol. 1, 3rd edition, 1951, page 743 et seq. and page 769 et seq. Preferably, a stirred catalyst cascade or a tube reactor is used for a continuous process.

SUMM . . . reactor with 1,3-butadiene or with the hydrocarbon mixture, if required, a part of the hydrogen cyanide and a novel hydrocyanation catalyst which may have been produced in situ and, if required, a solvent. Suitable solvents are those mentioned above for the preparation of the novel catalysts, preferably aromatic hydrocarbons, such as toluene or xylene, or tetrahydrofuran.

SUMM . . . extraction, and working-up of the remaining reaction mixture by distillation to isolate the desired products and recover the still active catalyst.

SUMM . . . and hydrocyanic acid are fed to a reactor via separate feeds at the rate at which they are consumed. The catalysts can be fed in together with one of the starting materials or via a separate feed. Suitable, preferably thoroughly mixable reactors are likewise known to a person skilled in the art. They include, for example, stirred catalysts, catalytic cascades and tube reactors, which, if required, are provided with an internal lining. The working-up of the reaction products, too, . . .

SUMM . . . an isomerization additionally takes place at higher reaction temperatures and/or during longer reaction times in the presence of the novel catalysts, the 3-pentenenitrile/2-methyl-3-butenenitrile ratio obtained then generally being about 2:1, preferably about 5:1, in particular about 8:1.

SUMM . . . fraction of 3-pentenenitrile or 4-pentenenitrile and a very small fraction of conjugated 2-pentenenitrile and 2-methyl-2-butenenitrile which may act as a catalyst poison should be formed.

SUMM The novel catalysts based on phosphonite ligands are also advantageous for the positional and double bond isomerization in step 2 and/or the addition. . .

SUMM The present invention therefore furthermore relates to a process for the catalytic isomerization of branched aliphatic monoalkenenitriles having a nonconjugated C.dbd.C and C.tbd.N bond to give linear monoalkenenitriles, wherein the isomerization is carried out in the presence of a novel catalyst.

SUMM . . . aliphatic, nonconjugated 2-alkyl-3-monoalkenenitriles and in particular 2-methyl-3-butenenitrile. Mixtures of monoolefinic C.sub.5-mononitriles, as obtainable by the process, described above, for the catalytic hydrocyanation of butadiene or of 1,3-butadiene-containing hydrocarbon mixtures, are preferably used for the isomerization. Advantageously, the novel catalysts exhibit good activity with respect to the formation of linear monoalkene nitrates. The isomerization can, if desired, be effected in the presence of a

- conventional promoter, for example a Lewis acid, such as AlCl₃.sub.3 or ZnCl₂.sub.2. Advantageously, the novel catalysts generally permit isomerization without the addition of a promoter. The selectivity of the novel catalysts in the isomerization without the addition of a promoter is in general higher than that with the addition of a promoter. Furthermore, expensive removal of the promoter of the isomerization can be dispensed with. Thus, in principle only one catalyst circulation for hydrocyanation, isomerization and, if required, an addition reaction of a second molecule of hydrogen cyanide is required. Dispensing. . .
- SUMM The present invention furthermore relates to a process for the preparation of adipodinitrile by catalytic hydrocyanation of linear monoolefinic C.sub.5-mononitriles, wherein the hydrocyanation is carried out in the presence of a novel catalyst. Advantageously, a mixture of monoolefinic C.sub.5-mononitriles which is obtainable by the novel process for the catalytic hydrocyanation of butadiene or of a 1,3-butadiene-containing hydrocarbon mixture and which, if required, was additionally subjected to working up and/or. . .
- SUMM In a suitable embodiment of the novel process for the preparation of adipodinitrile, the catalytic hydrocyanation of butadiene or of a 1,3-butadiene-containing hydrocarbon mixture (Step 1) and the isomerization (Step 2) are carried out in. . . separate reactors, where, for example, after the end of the monoaddition reaction of hydrogen cyanide in a first reactor, the catalyst-containing reaction mixture is transferred, without isolation and working up, to a second reactor and is isomerized therein.
- SUMM a) preparation of a mixture of monoolefinic C.sub.5-mononitriles having a nonconjugated C.dbd.C and C.tbd.N bond by catalytic hydrocyanation of butadiene or of a 1,3-butadiene-containing hydrocarbon mixture,
- SUMM b) catalytic isomerization of the mixture from a), and
- SUMM c) catalytic hydrocyanation of the isomerized mixture from b), wherein the steps a), b) and c) are carried out in the presence of at least one novel catalyst and without isolation of the product or products from step a) and/or b).
- SUMM The novel catalysts can be prepared simply and thus economically from readily obtainable intermediates, some of which are commercially available. Advantageously, they have. . . in the hydrocyanation of 1,3-butadiene-containing hydrocarbon mixtures. In general, they have higher stability relative to hydrogen cyanide than conventional hydrocyanation catalysts and, in the hydrocyanation, an excess of hydrogen cyanide can also be added to said catalysts without resulting in marked deposition of inactive nickel(II) compounds, e.g. nickel(II) cyanide. In contrast to known hydrocyanation catalysts based on non-complex phosphine and phosphite ligands, the novel catalysts are therefore suitable not only for continuous hydrocyanation processes in which an excess of hydrogen cyanide in the reaction mixture. . . also for semicontinuous processes and batch processes in which a large excess of hydrogen cyanide is generally present. Thus, the catalysts used according to the invention and the hydrocyanation processes based on them generally have higher catalyst recycling rates and longer catalyst on-stream times than known processes. This is advantageous not only for achieving better cost-efficiency but also from ecological points of view, since the nickel cyanide formed from the active catalyst with hydrogen cyanide is highly toxic and must be worked up or disposed of at high cost. Moreover, in the preparation of the novel catalysts, generally no excess or a smaller excess of ligand is required relative to the metal of subgroup VIII than in the case of conventional catalysts.
- SUMM In addition to the hydrocyanation of 1,3-butadiene-containing hydrocarbon mixtures, the catalysts of the formula I are generally suitable for all conventional hydrocyanation processes. In particular,

- SUMM the hydrocyanation of nonactivated olefins, for . . .
 SUMM The catalysts which are described above and comprise chiral phosphonite ligands of the formula I are suitable for enantioselective hydrocyanation.
- DETD 0.41 g (1.5 mmol) of bis(1,5-cyclooctadienyl)nickel(0), 2.14 g of ligand I and 10 ml of toluene are initially taken under argon at room temperature in a glass autoclave and stirred for 10 minutes, the reaction batch acquiring a red-brown color. A. . .
- DETD . . . g (1.5 mmol) of bis(1,5-cyclooctadienyl)nickel(0), 2.9 g of ligand II and 10 g of toluene are initially taken under an argon atmosphere at room temperature in a glass autoclave and stirred for 10 minutes, the reaction batch acquiring a red-brown color.. . .
- DETD . . . g of ligand I, 15 ml of toluene and 0.14 g (0.5 mmol) of bis(1,5-cyclooctadienyl)nickel(0) are initially taken under an argon atmosphere and stirred at room temperature for 45 minutes. The catalyst complex which forms is precipitated from the initially homogeneous solution. The volatile components are removed at highly superatmospheric pressure. 40.5. . .
- DETD As demonstrated by Example 3, isomerization using the novel catalysts is also possible without the addition of a promoter.
- DETD . . . g of ligand II, 8 ml of toluene and 0.07 g (0.25 mmol) of bis(1,5-cyclooctadienyl)nickel(0) are initially taken under an argon atmosphere and stirred at room temperature for 30 minutes. Some of the catalyst complex which forms is precipitated from the initially red homogeneous solution. The volatile components are removed at highly superatmospheric pressure.. . .
- CLM What is claimed is:
1. A catalyst composition comprising a complex of a metal of group VIII, and a bidentate phosphonite ligand of the formula I ##STR10##. . .
 2. The catalyst composition as claimed in claim 1, A being a radical of the formulae II.1 to II-5 ##STR11## where X is. . .
 3. The catalyst composition as claimed in claim 1, R.sup.1 and R.sup.1', independently of one another, being alkyl or aryl.
 4. The catalyst composition as claimed in claim 1, R.sup.2 and R.sup.2', independently of one another, each being phenyl substituents which may have. . .
 5. The catalyst composition as claimed in claim 1, the phosphonite ligand of the formula I being selected from ligands of the formulae. . .
 6. The catalyst composition as claimed in claim 1, which additionally has at least one further ligand selected from cyanide, halides, amines, carboxylates,. . .
 7. The catalyst composition as claimed in claim 1, the metal of group VIII being cobalt, rhodium, ruthenium, palladium or nickel.
 - . . . 9. A process for the preparation of a mixture of monoolefinic C.sub.5-mononitriles having a nonconjugated C.dbd.C and C.tbd.N bond by catalytic hydrocyanation of butadiene or of a 1,3-butadiene-containing hydrocarbon mixture, wherein the hydrocyanation is carried out in the presence of a catalyst composition as claimed in claim 1.
 10. A process for the catalytic isomerization of branched aliphatic monoalkenenitriles having a nonconjugated C.dbd.C and C.tbd.N bond to give linear monoalkenenitriles, wherein the isomerization is carried out in the presence of a catalyst composition as claimed in claim 1.
 11. A process for the preparation of adipodinitrile by catalytic hydrocyanation of a linear monoolefinic C.sub.5-mononitrile, wherein the

hydrocyanation is carried out in the presence of a catalyst composition as claimed in claim 1.

- · preparation of adipodinitrile, comprising a) preparation of a mixture of monoolefinic C.sub.5-mononitriles having a nonconjugated C.dbd.C and C.tbd.N bond by catalytic hydrocyanation of butadiene or of a 1,3-butadiene-containing hydrocarbon mixture, b) catalytic isomerization of the mixture from a), and c) catalytic hydrocyanation of the isomerized mixture from b), wherein the steps a), b) and c) are carried out in the presence of at least one catalyst composition as claimed in claim 1 and without isolation of the product or products from step a) and/or b).
- · of olefins, wherein the hydrocyanation and/or positional and double-bond isomerization of olefins is carried out in the presence of a catalyst composition as claimed in claim 1.

14. The catalyst composition as claimed in claim 3, wherein R.sup.1 and R.sup.1', independently of one another, are selected from the group consisting. . .

IT 74-90-6, Hydrocyanic acid, reactions

(hydrocyanation of butadiene; group VIII metal complex catalyst with bidentate phosphonite ligand and manufacture of alkenenitriles)

IT 106-99-0, 1,3-Butadiene, reactions

(hydrocyanation; group VIII metal complex catalyst with bidentate phosphonite ligand and manufacture of alkenenitriles)

IT 4635-87-4P, 3-Pentenenitrile 16529-56-9P, 2-Methyl-3-butenenitrile

(manufacture and isomerization; group VIII metal complex catalyst with bidentate phosphonite ligand and manufacture of alkenenitriles)

TI Catalyst comprising a complex of a metal from subgroup VIII based on a bidentate phosphonite ligand, and method for producing nitriles|

PI US 6521778 B1 20030218

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WO 9964155 19991216|

AB A catalyst which comprises at least one complex of a metal of subgroup VIII having at least one bidentate phosphonite ligand of the formula I ##STR1##| or salts and mixtures thereof, a process for the preparation of mixtures of monoolefinic C.sub.5-mononitriles, a process for the catalytic isomerization of branched aliphatic monoalkenenitriles and a process for the preparation of adiponitrile.|

SUMM The present invention relates to a catalyst which comprises a complex of a metal of subgroup VIII, which comprises at least one bidentate phosphonite ligand, a process for the preparation of mixtures of monoolefinic C.sub.5-mononitriles and a process for the preparation of adipodinitrile by catalytic hydrocyanation in the presence of such a catalyst.

SUMM "Applied Homogeneous Catalysis with Organometallic Compounds", Vol. 1, VCH Weinheim, page 465 et seq., describes in general the addition reaction of hydrogen cyanide with olefins under heterogeneous and homogeneous catalysis. In particular, catalysts based on phosphine, phosphite and phosphinite complexes of nickel and of palladium are used. For the preparation of adiponitrile by hydrocyanation of butadiene, predominantly nickel(0) phosphite catalysts are used, in the presence or absence of a Lewis acid as a promoter.

SUMM J. Chem. Soc., Chem. Commun., 1991, page 1292, describes chiral aryl diphosphites as ligands for hydrocyanation catalysts. In these ligands, the phosphite group is bonded via two of its oxygen atoms to the 3- and 3'-positions of a 2,2'-binaphthyl unit, with which it thus

forms a 7-membered heterocycle. In addition, two of these heterocycles may likewise be linked via a 2,2'-binaphthyl unit to form a bidentate chelate ligand. In J. Chem. Soc., Chem. Commun., 1991, page 803 et seq., analogous chelate diphosphite complexes of nickel(0) and platinum(0) are described for this purpose, a 2,2'-biphenyl unit being used instead of a 2,2'-binaphthyl unit as the bridging group.

- SUMM U.S. Pat. No. 5,449,807 describes a process for the gas-phase hydrocyanation of diolefins in the presence of a supported nickel catalyst based on at least one bidentate phosphite ligand, the two phosphite groups being bridged by an unsubstituted or substituted 2,2'-biphenyl group. U.S. Pat. No. 5,440,067 describes a process for the gas-phase isomerization of 2-alkyl-3-monoalkenenitriles to give linear 3- and/or 4-monoalkenenitriles in the presence of the catalysts described in U.S. Pat. No. 5,449,807.
- SUMM WO 95/14659 describes a process for the hydrocyanation of monoolefins, in which catalysts based on zero-valent nickel and bidentate phosphite ligands may be used. In these ligands, the phosphite groups together with two of their oxygen atoms are part of an aryl-fused 7-membered heterocycle. Pairs of these phosphite groups are then bridged by aryl-fused alkylene groups via the oxygen atoms which are not part of the heterocycle.
- SUMM U.S. Pat. No. 5,512,695 likewise describes a process for the hydrocyanation of monoolefins in the presence of a nickel catalyst which comprises a bidentate phosphite ligand.
- SUMM WO 96/11182 describes a process for hydrocyanation in the presence of a nickel catalyst based on a bidentate or polydentate phosphite ligand in which the phosphite groups are not part of a heterocycle. The groups used for bridging the phosphite groups correspond to those described in WO 95/14659.
- SUMM U.S. Pat. No. 5,523,453 describes a process for hydrocyanation in the presence of a nickel catalyst based on a bidentate ligand which comprises at least one phosphinite group and a further phosphorus-containing group which is selected from phosphinites and phosphites. The two phosphorus-containing groups of these bidentate ligands are in turn bridged via aryl-fused groups. WO 97/23446 describes a process for the hydrocyanation of diolefins and for the isomerization of 2-alkyl-3-monoalkenenitriles in the presence of catalysts which correspond to those described in U.S. Pat. No. 5,523,453.
- SUMM WO 96/22968 likewise describes a process for the hydrocyanation of diolefinic compounds and for the isomerization of the resulting, nonconjugated 2-alkyl-3-monoalkenenitriles, a nickel(0) catalyst based on a polydentate phosphite ligand being used in the presence of a Lewis acid as promoter. The phosphite groups of these polydentate ligands are once again components of aryl-fused heterocycles and may be bridged via aryl-fused groups.
- SUMM None of the abovementioned publications describes hydrocyanation catalysts based on phosphonite ligands. In particular, no catalysts based on bidentate chelate phosphonites are described.
- SUMM U.S. Pat. No. 3,766,237 describes a process for the hydrocyanation of ethylenically unsaturated compounds which may have further functional groups, such as nitriles, in the presence of a nickel catalyst. These nickel catalysts carry four ligands of the formula M(X,Y,Z), where X,

Y and Z, independently of one another, are each a radical R or OR and R is selected from alkyl and aryl groups of up to 18 carbon atoms. However, only phosphines and phosphites are mentioned explicitly and are used in the examples for the hydrocyanation. On the other hand, it is not disclosed that phosphonites can be used as ligands for nickel(0) hydrocyanation catalysts. In particular, no bidentate chelate phosphonite ligands are described.

- SUMM It is an object of the present invention to provide novel catalysts based on a metal of subgroup VIII. They should preferably have good selectivity and good catalytic activity in the hydrocyanation of 1,3-butadiene and 1,3-butadiene-containing hydrocarbon mixtures. Preferably, they should also be suitable for the catalytic isomerization of monoalkenenitriles and for the addition reaction of the second molecule of hydrogen cyanide with said monoalkenenitriles, for example for the preparation of adipodinitrile.
- SUMM We have surprisingly found that this object is achieved by catalysts based on a metal of subgroup VIII which comprise at least one bidentate phosphonite ligand.
- SUMM The present invention therefore relates to a catalyst comprising a complex of a metal of subgroup VIII, having a bidentate phosphonite ligand of the formula I ##STR2##
- SUMM The novel catalysts may have one or more of the phosphonite ligands of the formula I. In addition to the ligands of formula I which are described above, they may also have at least one further ligand which is selected from cyanide, halides, amines, carboxylates, acetylacetone, arylsulfonates, alkanesulfonates, hydride, CO, olefins, dienes, cycloolefins, nitrites, N-containing heterocycles, aromatics and heteroaromatics, ethers, PF₃ and mono-, bi- and polydentate phosphine, phosphinite, phosphonite and phosphite ligands. These further ligands may likewise be mono-, bi- or polydentate and may have coordinate bonds to the metal of subgroup VIII. Suitable further phosphorus-containing ligands are, for example, the phosphine, phosphinite and phosphite ligands described above as prior art.
- SUMM Preferably, the metal of subgroup VIII is cobalt, rhodium, ruthenium, palladium or nickel. If the novel catalysts are used for hydrocyanation, the metal of subgroup VIII is in particular nickel.
- SUMM For the preparation of the phosphonite ligands of the formula I which are used in the novel catalysts, a dihalophosphorus(III) compound III, where R^{sup.1} (or R^{sup.1'}) has the abovementioned meanings, can first be reacted with a monoalcohol IV, where R^{sup.2} (or R^{sup.2'}) has the abovementioned meanings, to give a compound of the formula V, according to the following scheme. If desired, this compound V can be isolated and/or purified by known methods, e.g. by distillation, before the further reaction. The compound V is then reacted with a diol of the formula VI to give the bidentate phosphonite ligands of the formula (I). Where, in the formula (I), R^{sup.1} is identical to R^{sub.1'} and R^{sup.2} is identical to R^{sup.2'}, two equivalents of the formula V can be reacted with one equivalent of the formula VI in a one-stage reaction. Otherwise, first one equivalent of the formula V is reacted with one equivalent of the formula VI and, after formation of the monocondensate, a second compound of the formula (V) Cl-PR^{sup.1}--OR^{sup.2} is added and is further reacted to give the phosphonite of the formula (I). ##STR8##

- SUMM For the preparation of the novel catalysts, at least one phosphonite ligand of the formula I can be reacted with a metal of subgroup VIII, e.g. nickel, or with a compound of the metal in the presence of a reducing agent or a complex of the metal, in each case in an inert solvent. Suitable nickel compounds of, for example, compounds in which the transition metal assumes an oxidation state higher than 0 and which are reduced in situ during the reaction with the phosphonite ligand of the formula I, in the presence or absence of a suitable reducing agent. These include, for example, the halides, preferably the chlorides, and the acetates of the abovementioned transition metals. NiCl₂.sub.2 is preferably used. Suitable reducing agents are, for example, metals, preferably alkali metals, such as Na and K, aluminum, zinc and trialkylaluminum compounds.
- SUMM Suitable inert solvents for the preparation of the nickel(0) complexes are, for example, aromatics, such as benzene, toluene, ethylbenzene and chlorobenzene, ethers, preferably diethyl ether and tetrahydrofuran, and haloalkanes, for example dichloromethane, chloroform, dichloroethane and trichloroethane. Other suitable solvents are the liquid starting materials and/or products of the catalyzed reaction. The temperature is from -70 to 150°C., preferably from 0°C. to 100°C., particularly preferably about room temperature.
- SUMM If elemental nickel is used for the preparation of the phosphonite-nickel(0) complexes, it is preferably in the form of a powder. The reaction of nickel and phosphonite ligand is preferably effected in a product of the catalyzed reaction, such as the hydrocyanation reaction, as the solvent, for example in a mixture of monoolefinic C_{sub.5}-mononitriles or, preferably, in 3-pentenenitrile or 2-methyl-3-butenenitrile. If required, the ligand may also be used as solvent. The temperature is from about 0 to 150°C., preferably 60 to 100°C.
- SUMM The present invention furthermore relates to a process for the preparation of mixtures of monoolefinic C_{sub.5}-mononitriles having a nonconjugated C.dbd.C and C.tbd.N bond by catalytic hydrocyanation of butadiene or of a 1,3-butadiene-containing hydrocarbon mixture, wherein the hydrocyanation is carried out in the presence of at least one of the novel catalysts described above.
- SUMM C_{sub.4} cuts are, if required, essentially freed from 1,2-dienes, such as propadiene, and from alkynes, e.g. vinylacetylene, before the hydrocyanation of alkynes, such as propyne or butyne. Otherwise, products may be obtained in which a C.dbd.C double bond is present in conjugation with the C.tbd.N bond. These may act as catalyst poisons for the first reaction step of the adipic acid preparation, the monoaddition reaction of hydrogen cyanide.
- SUMM If required, those components which may give rise to catalyst poisons, in particular alkynes, 1,2-dienes and mixtures thereof, are therefore partially or completely removed from the hydrocarbon mixture. To remove these components, the C_{sub.4} cut is subjected to a partial catalytic hydrogenation before the addition reaction with hydrogen cyanide. This partial hydrogenation is effected in the presence of a hydrogenation catalyst which is capable of hydrogenating alkynes and 1,2-dienes selectively alongside other dienes and monoolefins.
- SUMM Suitable heterogeneous catalyst systems for the selective hydrogenation are known and comprise in general a transition metal compound on an inert support. They are in particular those described in

U.S. Pat. Nos. 4,587,369, 4,704,492 and 4,493,906, which are hereby fully incorporated by reference. Further suitable catalyst systems based on copper are sold by Dow Chemical as KLP catalyst.

- SUMM Suitable reactors for the reaction are known to a person skilled in the art and are described, for example, in Ullmanns Enzyklopädie der technischen Chemie, Vol. 1, 3rd edition, 1951, page 743 et seq. and page 769 et seq. Preferably, a stirred catalyst cascade or a tube reactor is used for a continuous process.
- SUMM a) Filling a reactor with 1,3-butadiene or with the hydrocarbon mixture, if required, a part of the hydrogen cyanide and a novel hydrocyanation catalyst which may have been produced in situ and, if required, a solvent. Suitable solvents are those mentioned above for the preparation of the novel catalysts, preferably aromatic hydrocarbons, such as toluene or xylene, or tetrahydrofuran.
- SUMM c) If required, completion of the reaction by continued reaction and subsequent working up. To complete the reaction, the reaction time may be followed by a subsequent reaction time of from 0 minutes to about 5 hours, preferably from about 1 hour to 3.5 hours, in which hydrogen cyanide is no longer fed into the autoclaves. The temperature is left essentially constant at the previously set reaction temperature during this time. Working up is effected by conventional methods and comprises the removal of the unconverted 1,3-butadiene and of the unconverted hydrogen cyanide, for example by washing or extraction, and working-up of the remaining reaction mixture by distillation to isolate the desired products and recover the still active catalyst.
- SUMM The addition reaction of the hydrogen cyanide with 1,3-butadiene or a 1,3-butadiene-containing hydrocarbon mixture is preferably carried out continuously. The reaction is generally carried out so that essentially no relatively large amounts of unconverted hydrogen cyanide are present in the reactor. Suitable processes for the continuous hydrocyanation are known to a person skilled in the art. They include, for example, a feed process in which 1,3-butadiene and hydrocyanic acid are fed to a reactor via separate feeds at the rate at which they are consumed. The catalysts can be fed in together with one of the starting materials or via a separate feed. Suitable, preferably thoroughly mixable reactors are likewise known to a person skilled in the art. They include, for example, stirred catalysts, catalytic cascades and tube reactors, which, if required, are provided with an internal lining. The working-up of the reaction products, too, is preferably carried out by a conventional continuous method.
- SUMM In general, the 3-pentenenitrile/2-methyl-3-butenenitrile ratio obtained in the monoaddition reaction of hydrogen cyanide with 1,3-butadiene or the 1,3-butadiene-containing hydrocarbon mixture immediately after the end of the addition reaction (unconverted hydrogen cyanide no longer present) is at least 0.4:1. Advantageously, an isomerization additionally takes place at higher reaction temperatures and/or during longer reaction times in the presence of the novel catalysts, the 3-pentenenitrile/2-methyl-3-butenenitrile ratio obtained then generally being about 2:1, preferably about 5:1, in particular about 8:1.
- SUMM 2. Isomerization of the 2-methyl-3-butenenitrile contained in these mixtures to give 3-pentenenitrile and isomerization of the 3-pentenenitrile thus formed and of the 3-pentenenitrile already contained from step 1 to give various n-pentenenitriles. A very high fraction of 3-pentenenitrile or 4-pentenenitrile and a very small

fraction of conjugated 2-pentenenitrile and 2-methyl-2-butenenitrile which may act as a catalyst poison should be formed.

- SUMM The novel catalysts based on phosphonite ligands are also advantageous for the positional and double bond isomerization in step 2 and/or the addition reaction of the second molecule of hydrogen cyanide in step 3.
- SUMM The present invention therefore furthermore relates to a process for the catalytic isomerization of branched aliphatic monoalkenenitriles having a nonconjugated C.dbd.C and C.tbd.N bond to give linear monoalkenenitriles, wherein the isomerization is carried out in the presence of a novel catalyst.
- SUMM Suitable branched aliphatic monoalkenenitriles are preferably acyclic, aliphatic, nonconjugated 2-alkyl-3-monoalkenenitriles and in particular 2-methyl-3-butenenitrile. Mixtures of monoolefinic C._{sub}.5-mononitriles, as obtainable by the process, described above, for the catalytic hydrocyanation of butadiene or of 1,3-butadiene-containing hydrocarbon mixtures, are preferably used for the isomerization. Advantageously, the novel catalysts exhibit good activity with respect to the formation of linear monoalkene nitriles. The isomerization can, if desired, be effected in the presence of a conventional promoter, for example a Lewis acid, such as AlCl._{sub}.3 or ZnCl._{sub}.2. Advantageously, the novel catalysts generally permit isomerization without the addition of a promoter. The selectivity of the novel catalysts in the isomerization without the addition of a promoter is in general higher than that with the addition of a promoter. Furthermore, expensive removal of the promoter of the isomerization can be dispensed with. Thus, in principle only one catalyst circulation for hydrocyanation, isomerization and, if required, an addition reaction of a second molecule of hydrogen cyanide is required. Dispensing with the promoter and simplification of the process which is possible in principle generally permit a reduction of the costs compared with known processes.
- SUMM The present invention furthermore relates to a process for the preparation of adipodinitrile by catalytic hydrocyanation of linear monoolefinic C._{sub}.5-mononitriles, wherein the hydrocyanation is carried out in the presence of a novel catalyst. Advantageously, a mixture of monoolefinic C._{sub}.5-mononitriles which is obtainable by the novel process for the catalytic hydrocyanation of butadiene or of a 1,3-butadiene-containing hydrocarbon mixture and which, if required, was additionally subjected to working up and/or to isomerization by the novel isomerization process described above is used for the hydrocyanation. In a suitable embodiment of the novel process, the hydrocyanation of the monoolefinic C._{sub}.5-mononitriles is carried out in the presence of a promoter, for example a Lewis acid, such as AlCl._{sub}.3, ZnCl._{sub}.2, BF._{sub}.3, B(C._{sub}.6H._{sub}.5)._{sub}.3, SnCl._{sub}.4, Sn(C._{sub}.6H._{sub}.5)._{sub}.3OSO._{sub}.2CF._{sub}.3, etc.
- SUMM In a suitable embodiment of the novel process for the preparation of adipodinitrile, the catalytic hydrocyanation of butadiene or of a 1,3-butadiene-containing hydrocarbon mixture (Step 1) and the isomerization (Step 2) are carried out in the manner of a one-pot reaction without isolation of the hydrocyanation products. Hydrocyanation and isomerization can be carried out, for example, in one reactor, the reaction temperature being increased, if required, after the end of the hydrogen cyanide addition. Hydrocyanation and isomerization can also be carried out in separate reactors, where, for example, after the end of the monoaddition reaction of hydrogen cyanide in a first reactor, the catalyst-containing reaction mixture is

transferred, without isolation and working up, to a second reactor and is isomerized therein.

- SUMM a) preparation of a mixture of monoolefinic C_{sub}.5-mononitriles having a nonconjugated C_{dbd}.C and C_{tbd}.N bond by catalytic hydrocyanation of butadiene or of a 1,3-butadiene-containing hydrocarbon mixture,
- SUMM b) catalytic isomerization of the mixture from a), and
- SUMM c) catalytic hydrocyanation of the isomerized mixture from b), wherein the steps a), b) and c) are carried out in the presence of at least one novel catalyst and without isolation of the product or products from step a) and/or b).
- SUMM The novel catalysts can be prepared simply and thus economically from readily obtainable intermediates, some of which are commercially available. Advantageously, they have high activity and good selectivity with respect to the monoadducts or isomerization products obtained in the hydrocyanation of 1,3-butadiene-containing hydrocarbon mixtures. In general, they have higher stability relative to hydrogen cyanide than conventional hydrocyanation catalysts and, in the hydrocyanation, an excess of hydrogen cyanide can also be added to said catalysts without resulting in marked deposition of inactive nickel(II) compounds, e.g. nickel(II) cyanide. In contrast to known hydrocyanation catalysts based on non-complex phosphine and phosphite ligands, the novel catalysts are therefore suitable not only for continuous hydrocyanation processes in which an excess of hydrogen cyanide in the reaction mixture can generally be effectively avoided but also for semicontinuous processes and batch processes in which a large excess of hydrogen cyanide is generally present. Thus, the catalysts used according to the invention and the hydrocyanation processes based on them generally have higher catalyst recycling rates and longer catalyst on-stream times than known processes. This is advantageous not only for achieving better cost-efficiency but also from ecological points of view, since the nickel cyanide formed from the active catalyst with hydrogen cyanide is highly toxic and must be worked up or disposed of at high cost. Moreover, in the preparation of the novel catalysts, generally no excess or a smaller excess of ligand is required relative to the metal of subgroup VIII than in the case of conventional catalysts.
- SUMM In addition to the hydrocyanation of 1,3-butadiene-containing hydrocarbon mixtures, the catalysts of the formula I are generally suitable for all conventional hydrocyanation processes. In particular, the hydrocyanation of nonactivated olefins, for example of styrene and 3-pentenenitrile, may be mentioned.
- SUMM The catalysts which are described above and comprise chiral phosphonite ligands of the formula I are suitable for enantioselective hydrocyanation.
- DETD 0.41 g (1.5 mmol) of bis(1,5-cyclooctadienyl)nickel(0), 2.14 g of ligand I and 10 ml of toluene are initially taken under argon at room temperature in a glass autoclave and stirred for 10 minutes, the reaction batch acquiring a red-brown color. A mixture of 7.9 g (146 mmol) of 1,3-butadiene and 40 g of toluene is then added. The glass autoclave is tightly closed and the reaction mixture is heated to 70° C., an initial pressure of 1.2 bar being established. A mixture of 3.2 g (118 mmol) of freshly distilled hydrocyanic acid in 40 g of toluene is continuously metered in over a period of 90 minutes.

Thereafter, the pressure has fallen to 0.5 bar. The reaction is then completed in the course of a further 120 minutes at about 70° C. Toluene is used for washing the reaction discharge. The course of the reaction is monitored by pressure and temperature measurement.

DETD 0.41 g (1.5 mmol) of bis(1,5-cyclooctadienyl)nickel(0), 2.9 g of ligand II and 10 g of toluene are initially taken under an argon atmosphere at room temperature in a glass autoclave and stirred for 10 minutes, the reaction batch acquiring a red-brown color. A mixture of 8.1 g (150 mmol) of 1,3-butadiene and 40 g of toluene is then added. The glass autoclave is tightly closed and the reaction mixture is heated to 90° C. A mixture of 4.0 g of freshly distilled hydrocyanic acid in 40 g of toluene is metered in continuously over a period of 90 minutes. After the end of the addition, the temperature is increased to 110° C. The course of the isomerization (ratio of 3-pentenenitrile to 2-methyl-3-butenenitrile) is investigated at regular intervals (0, 3, 6, 22 h) by means of GC analysis, as described in Example 1. The results are shown in Table 1.

DETD 0.72 g of ligand I, 15 ml of toluene and 0.14 g (0.5 mmol) of bis(1,5-cyclooctadienyl)nickel(0) are initially taken under an argon atmosphere and stirred at room temperature for 45 minutes. The catalyst complex which forms is precipitated from the initially homogeneous solution. The volatile components are removed at highly superatmospheric pressure. 40.5 g (500 mmol) of 2-methyl-3-butenenitrile are added to the remaining solid. The solution is heated to 110° C. The course of the reaction is investigated at regular intervals by means of a gas chromatograph. The product ratio after a reaction time of 300 minutes is shown in Table 2. All products and by-products shown there were assigned beforehand by means of gas chromatography, GC-MS, GC-MS-IR and NMR. All values are in GC percent by area.

DETD As demonstrated by Example 3, isomerization using the novel catalysts is also possible without the addition of a promoter.

DETD 0.39 g of ligand II, 8 ml of toluene and 0.07 g (0.25 mmol) of bis(1,5-cyclooctadienyl)nickel(0) are initially taken under an argon atmosphere and stirred at room temperature for 30 minutes. Some of the catalyst complex which forms is precipitated from the initially red homogeneous solution. The volatile components are removed at highly superatmospheric pressure. 20.2 g (250 mmol) of 2-methyl-3-butenenitrile are added to the remaining solid. The solution is heated to 125° C. The course of the reaction is investigated at regular intervals by means of a gas chromatograph. The product ratio after a reaction time of 300 minutes is shown in Table 3. All products and by-products shown there were assigned beforehand by means of gas chromatography, GC-MS, GC-MS-IR and NMR. All values are in GC percent by area.

1. A catalyst composition comprising a complex of a metal of group VIII, and a bidentate phosphonite ligand of the formula I ##STR10## where A is a C.sub.2- to C.sub.7-alkylene bridge which may have 1, 2 or 3 double bonds and/or 1, 2 or 3 substituents which are selected from alkyl, cycloalkyl and aryl, it being possible for the aryl substituent additionally to carry 1, 2 or 3 substituents which are selected from alkoxy, halogen, trifluoromethyl, nitro, alkoxy carbonyl and cyano, and/or the C.sub.2- to C.sub.7-alkylene bridge may be interrupted by 1, 2 or 3 non-neighboring, unsubstituted or substituted heteroatoms, and/or the C.sub.2- to C.sub.7-alkylene bridge may be fused with one, two or three aryl and/or hetaryl groups, it being possible for the fused aryl and hetaryl groups each to carry 1, 2 or 3 substituents which are selected from alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, acyl, halogen, trifluoromethyl, nitro, cyano, carboxyl, alkoxy carbonyl and NE.sup.1 E.sup.2, where E.sup.1 and E.sup.2 are identical or different and are each alkyl, cycloalkyl or aryl, R.sup.1 and R.sup.1',

independently of one another, are each alkyl, cycloalkyl, aryl or hetaryl, each of which may carry 1, 2 or 3 substituents which are selected from alkyl, cycloalkyl and aryl, R.sup.2 and R.sup.2', independently of one another, are each alkyl, cycloalkyl, aryl or hetaryl, it being possible for the aryl and hetaryl groups each to carry 1, 2 or 3 substituents which are selected from alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, acyl, halogen trifluoromethyl, nitro, cyano, carboxyl, alkoxy carbonyl and NE.sup.1E.sup.2, where E.sup.1 and E.sup.2 may have the abovementioned meanings, or a salt or mixture thereof.

2. The catalyst composition as claimed in claim 1, A being a radical of the formulae II.1 to II-5 ##STR11## where X is O, S or NR.sup.5, where R.sup.5 is alkyl, cycloalkyl or aryl, or X is a C.sub.1- to C.sub.3-alkylene bridge which may have a double bond and/or an alkyl, cycloalkyl or aryl substituent, wherein the aryl is optionally substituted by one, two or three substituents, which are selected from alkyl, alkoxy, halogen, trifluoromethyl, nitro, alkoxy carbonyl and cyano, or X is a C.sub.2- or C.sub.3-alkylene bridge which is interrupted by O, S or NR.sup.5, and R.sup.3, R.sup.3', R.sup.3", R.sup.3"', R.sup.4, R.sup.4', R.sup.4" and R.sup.4''' independently of one another, are each hydrogen, alkyl, alkoxy, halogen, trifluoromethyl, nitro, alkoxy carbonyl or cyano.

3. The catalyst composition as claimed in claim 1, R.sup.1 and R.sup.1', independently of one another, being alkyl or aryl.

4. The catalyst composition as claimed in claim 1, R.sup.2 and R.sup.2', independently of one another, each being phenyl substituents which may have one or two substituents which are selected from alkyl, alkoxy, halogen, trifluoromethyl, nitro, cyano, alkoxy carbonyl and carboxyl.

5. The catalyst composition as claimed in claim 1, the phosphonite ligand of the formula I being selected from ligands of the formulae Ia to Ic ##STR12## where, in the formula Ia, R.sup.3, R.sup.4, R.sup.7 and R.sup.8 have the following meanings:

R.sup.3 R.sup.4 R.sup.7 R.sup.8

H H H H
tert-butyl methyl H H
tert-butyl methoxy H H
H H methyl H
H H ethyl H
H H isopropyl H
H H tert-butyl H
H Cl H H
H CF₃ H H
H H methyl methoxy in the formula Ib, R.sup.4, R.sup.7, R.sup.8 and R.sup.9 have the following meanings

R.sup.4 R.sup.7 R.sup.8 R.sup.9

H H H H
Cl H H H
methoxy H H H
H H H phenyl
H methyl H H
H methyl methoxy H

H methyl methoxy phenyl in the formula Ic, R.sup.7 and R.sup.8 have the following meanings:

R.sup.7 R.sup.8

H H
methyl H
ethyl H
isopropyl H
tert-butyl H
methyl methoxy
i-propyl H
i-propyl methoxy
H Cl
H CF₃

6. The catalyst composition as claimed in claim 1, which additionally has at least one further ligand selected from cyanide, halides, amines, carboxylates, acetylacetone, arylsulfonates, alkanesulfonates, hydride, CO, olefins, dienes, cycloolefins, nitriles, N-containing heterocycles, aromatics and heteroaromatics, ethers, PF₃ and mono-, bi- and polydentate phosphine, phosphinite and phosphite ligands.

7. The catalyst composition as claimed in claim 1, the metal of group VIII being cobalt, rhodium, ruthenium, palladium or nickel.

9. A process for the preparation of a mixture of monoolefinic C_{sub.5}-mononitriles having a nonconjugated C.dbd.C and C.tbd.N bond by catalytic hydrocyanation of butadiene or of a 1,3-butadiene-containing hydrocarbon mixture, wherein the hydrocyanation is carried out in the presence of a catalyst composition as claimed in claim 1.

10. A process for the catalytic isomerization of branched aliphatic monoalkenenitriles having a nonconjugated C.dbd.C and C.tbd.N bond to give linear monoalkenenitriles, wherein the isomerization is carried out in the presence of a catalyst composition as claimed in claim 1.

11. A process for the preparation of adipodinitrile by catalytic hydrocyanation of a linear monoolefinic C_{sub.5}-mononitrile, wherein the hydrocyanation is carried out in the presence of a catalyst composition as claimed in claim 1.

12. A process for the preparation of adipodinitrile, comprising a) preparation of a mixture of monoolefinic C_{sub.5}-mononitriles having a nonconjugated C.dbd.C and C.tbd.N bond by catalytic hydrocyanation of butadiene or of a 1,3-butadiene-containing hydrocarbon mixture, b) catalytic isomerization of the mixture from a), and c) catalytic hydrocyanation of the isomerized mixture from b), wherein the steps a), b) and c) are carried out in the presence of at least one catalyst composition as claimed in claim 1 and without isolation of the product or products from step a) and/or b).

13. A process for the hydrocyanation and/or positional and double-bond isomerization of olefins, wherein the hydrocyanation and/or positional and double-bond isomerization of olefins is carried out in the presence of a catalyst composition as claimed in claim 1.

14. The catalyst composition as claimed in claim 3, wherein R.sup.1 and R.sup.1', independently of one another, are selected from the group consisting of phenyl,

IT 74-90-8, Hydrocyanic acid, reactions
 (hydrocyanation of butadiene; group VIII metal complex catalyst with bidentate phosphonite ligand and manufacture of alkenenitriles)
 IT 106-99-0, 1,3-Butadiene, reactions
 (hydrocyanation; group VIII metal complex catalyst with bidentate phosphonite ligand and manufacture of alkenenitriles)
 IT 4635-87-4P, 3-Pentenenitrile 16529-56-9P, 2-Methyl-3-butenenitrile
 (manufacture and isomerization; group VIII metal complex catalyst with bidentate phosphonite ligand and manufacture of alkenenitriles)
 IT 74-90-8, Hydrocyanic acid, reactions
 (hydrocyanation of butadiene; group VIII metal complex catalyst with bidentate phosphonite ligand and manufacture of alkenenitriles)
 RN 74-90-8 USPATFULL
 CN Hydrocyanic acid (CA INDEX NAME)



IT 106-99-0, 1,3-Butadiene, reactions
 (hydrocyanation; group VIII metal complex catalyst with bidentate phosphonite ligand and manufacture of alkenenitriles)
 RN 106-99-0 USPATFULL
 CN 1,3-Butadiene (CA INDEX NAME)



IT 4635-87-4P, 3-Pentenenitrile
 (manufacture and isomerization; group VIII metal complex catalyst with bidentate phosphonite ligand and manufacture of alkenenitriles)
 RN 4635-87-4 USPATFULL
 CN 3-Pentenenitrile (CA INDEX NAME)



L88 ANSWER 55 OF 60 USPATFULL on STN

ACCESSION . . .
 HCl to produce the phosphorus-containing polymer, which is then contacted with an aromatic diol. The composition can be used as catalyst, for example, for converting an unsaturated organic compound to a nitrile and isomerizing a nitrile.

CAS INDEXING IS AVAILABLE FOR . . .

AB . . . HCl to produce the phosphorus-containing polymer, which is then contacted with an aromatic diol. The composition can be used as catalyst,

- for example, for converting an unsaturated organic compound to a nitrile and isomerizing a nitrile.
- SUMM [0001] This invention relates to a polymeric phosphite composition and polymeric phosphite catalyst composition that can be useful for a variety of catalytic processes, to a process for producing the composition, and to a process for using the composition in the hydrocyanation of. . .
- SUMM [0002] Phosphorus-based ligands are ubiquitous in catalysis, finding use for a number of commercially important chemical transformations. Phosphorus-based ligands commonly encountered in catalysis include phosphines and phosphites. Monophosphine and monophosphite ligands are compounds which contain a single phosphorus atom which serves as a. . .
- SUMM [0003] Two industrially important catalytic reactions using phosphorus ligands of particular importance are olefin hydrocyanation and isomerization of branched nitrites to linear nitrites. Phosphite ligands. . .
- SUMM [0004] Recovery of the ligand and catalyst is important for a successful process. Typical separation procedures to remove the product(s) from the catalyst and ligand involve extraction with an immiscible solvent or distillation. It is usually difficult to recover the catalyst and ligand quantitatively. For instance, distillation of a volatile product from a non-volatile catalyst results in thermal degradation of the catalyst. Similarly, extraction results in some loss of catalyst into the product phase. For extraction, one would like to be able to tune the solubility of the ligand and catalyst to disfavor solubility in the product phase. These ligands and metals are often very expensive and thus it is important. . .
- SUMM [0005] One method to solve the problem of catalyst and product separation is to attach the catalyst to an insoluble support. Examples of this approach have been previously described, and general references on this subject can be. . . Chemistry, Pergamon Press, 1982, Chapter 55; and Beller, M., Cornils, B., Frohning, C. D., Kohlpaintner, C. W., Journal of Molecular Catalysis A, 104, 1995, 17-85 and Macromol. Symp. 1994, 80, 241. Specifically, monophosphine and monophosphite ligands attached to solid supports are described in these references. Bisphosphine ligands have also been attached to solid supports and used for catalysis, as described in for example U.S. Pat. No. 5,432,289; J. Mol. Catal. A, 1996, 112,217; and J. Chem. Soc., Chem.. . .
- SUMM [0007] There is always a need to develop a composition that can be used as or in a catalyst with substantially reduced loss during a catalytic reaction or separation of product from the catalyst. An object of the present invention is, therefore, to provide such a composition and to provide processes for making and. . .
- SUMM . . . weight and degree of branching can control the solubility of the composition. Another advantage of the invention is that the catalyst produced by the composition can be substantially recovered by filtration. Other objects and advantages of the present invention will become. . .
- SUMM [0010] According to a second embodiment of the invention, a composition that can be used as a catalyst is provided, which comprises (1) composition disclosed in the first embodiment, (2) a Group VIII metal selected from Ni, Co,. . .
- SUMM . . . to a sixth embodiment of the invention, a process is provided. The process comprises contacting, in the presence of a catalyst disclosed in the second embodiment of the invention, an unsaturated organic compound with a hydrogen cyanide-containing fluid under a condition. . .
- SUMM . . . According to a seventh embodiment of the invention, a process is provided. The process comprises contacting a nitrile with the

catalyst disclosed in the second embodiment of the invention to produce linear 3-alkenenitrile.

SUMM . . . skilled in the art. For example, the diacetal can be prepared by refluxing di(trimethylolpropane) with salicylaldehyde with oxalic acid as catalyst. For references for preparing acetal from acid catalyzed reaction of an aldehyde and an alcohol, see Tetrahedron, 1996, 14599; Tet. Lett., 1989, 1609; Tetrahedron, 1990, 3315. 1,3-bis(2-hydroxyphenoxy)propane was. . .

SUMM . . . and degree of branching. For soluble polymeric system, separation can therefore be done by extraction. With insoluble polymeric systems, the catalyst can be placed in fixed beds or separated by filtration from a reaction mixture. Alternatively, the solubility of the polymer. . . reactants and insoluble in the products. Thus, the reaction can be carried out homogeneously to obtain high conversion. The polymeric catalyst can then be separated by easy means such as decantation or filtration.

SUMM . . . the compositions disclosed above can be combined with a Group VIII metal and, optionally, a Lewis acid to produce a catalyst composition. The term "Group VIII" refers to the ACS version of the Periodic Table of the Elements, 67.sup.th edition (1986-1987), . . . [0067] Generally, a Group VIII compound is combined with a polymer disclosed above to produce a desired catalyst. Among the Group VIII compounds, a nickel compound, a cobalt compound, or a palladium compound is preferred. A nickel compound. . .

SUMM . . . metal aluminum hydrides, metal alkyls, Li, Na, K, or H.sub.2. Elemental nickel, preferably nickel powder, when combined with a halogenated catalyst, as described in U.S. Pat. No. 3,903,120, is also a suitable source of zero-valent nickel.

SUMM . . . The amount of transition metal can be any amount so long as favorable results can be obtained with respect to catalyst activity and process economy, when used as a catalyst. In general, the molar ratio of phosphorus ligand to transition metal generally can be from about 1:1 to about 100:1. . .

SUMM . . . invention can further comprise one or more Lewis acid promoters that affect both the activity and the selectivity of the catalyst system. The promoter can be an inorganic or organometallic compound in which the promoter contains at least one element selected. . . alkyl or aryl group). U.S. Pat. No. 4,874,884 describes how synergistic combinations of promoters can be chosen to increase the catalytic activity of the catalyst system. Preferred promoters include CdCl₂.sub.2, FeCl₂.sub.2, ZnCl₂.sub.2, B(C₂H₅)₂.sub.3, and (C₂H₅)₂.sub.5SnX, where X=CF₃.sub.3SO₂.sub.3, CH₂.sub.3C. sub.2.6H₅.sub.5SO₂.sub.3, or (C₂H₅)₂.sub.5BCN. The mole ratio of promoter. . .

SUMM . . . compound conversions is provided. The process can comprise, consist essentially of, or consist of contacting, in the presence of a catalyst composition, an unsaturated organic compound with a hydrogen cyanide-containing fluid under a condition sufficient to produce a nitrile wherein the catalyst composition can be the same as that disclosed in the second embodiment of the invention. The term "fluid" can be. . .

SUMM . . . unsaturated organic compound can also be substituted with one or more functional groups containing a heteroatom, such as oxygen, sulfur, nitrogen or phosphorus. Examples of these heteroatom-substituted ethylenically unsaturated organic compounds include vinyl methyl ether, methyl oleate, oleyl alcohol, 3-pentenenitrile, 4-pentenenitrile, . . .

SUMM . . . process can be carried out, for example, by charging a suitable vessel such as a reactor with an unsaturated compound, catalyst composition, and solvent, if any to form a reaction mixture. Hydrogen

cyanide can be initially combined with other components to. . .

SUMM [0099] Another suitable technique is to charge the vessel with the catalyst and the solvent to be used, and feed both the unsaturated compound and the HCN slowly to the reaction mixture.

SUMM [0100] The molar ratio of unsaturated compound to catalyst can be varied from about 10:1 to about 10000:1. The molar ratio of HCN to catalyst generally is varied from about 10:1 to 100,000:1, preferably 100:1 to 5,000:1, for a batch operation. In a continuous operation, such as when using a fixed bed catalyst type of operation, a higher proportion of catalyst can be used such as 5:1 to 100,000:1, preferably 100:1 to 5,000:1, HCN to catalyst.

SUMM . . . solvent, if used, can be liquid at the reaction temperature and pressure and inert towards the unsaturated compound and the catalyst. Suitable solvents include hydrocarbons such as benzene, xylene, or combinations thereof; ethers such as tetrahydrofuran (THF); nitriles such as acetonitrile,. . .

SUMM [0103] The exact temperature is dependent to a certain extent on the particular catalyst being used, the particular unsaturated compound being used and the desired rate. Normally, temperatures of from -25° C. to 200°. . .

SUMM . . . with "cyanobutene"). Suitable unsaturated compounds include unsubstituted hydrocarbons as well as hydrocarbons substituted with groups, which do not attack the catalyst, such as cyano. These unsaturated compounds include, but are not limited to, monoethylenically unsaturated compounds containing from 2 to 30. . .

SUMM . . . in the presence of one or more Lewis acid promoters that affect both the activity and the selectivity of the catalyst system. The promoter is the same as that disclosed above.

SUMM . . . to the triple bond of the cyano group. Suitable starting 2-alkyl-3-monoalkenenitriles can also carry groups that do not attack the catalyst, for example, another cyano group. Preferably, the starting 2-alkyl-3-monoalkenenitriles contain from 5 to 8 carbon atoms, excluding any additional substitution. . .

SUMM . . . in the presence of a solvent or diluent. Any solvent or diluent that is inert to or nondestructive of the catalyst can be used, however. Suitable solvents include, but are not limited to, aliphatic or aromatic hydrocarbons (hexane, cyclohexane, benzene), ethers. . .

SUMM [0123] A nonoxidizing environment is desirable in order to retard oxidative deactivation of the catalyst. Accordingly, an inert atmosphere, e.g., nitrogen, is preferably used, although air can be used if desired at the expense of loss of a proportion of the catalyst through oxidation.

SUMM . . . nonvolatile, whereas the 2-methyl-3-butenenitrile reactant and the linear pentenenitrile products are relatively volatile. Accordingly, in a continuous flow procedure, the catalyst can be a component of the flowing system in a completely liquid-phase operation. It can also be in a mobile. . .

SUMM [0126] The molar ratio of 2-alkyl-3-monoalkenenitrile to catalyst is generally greater than 1:1, usually in the range from about 5:1 to 20,000:1, preferably 100:1 to 5,000:1, for a. . .

DETD [0127] The following non-limiting, representative examples illustrate the process and catalyst compositions of this invention. All parts, proportions, and percentages are by weight, unless otherwise indicated. In each example, the following. . .

DETD [0129] A catalyst solution was prepared by warming 0.1 g Fascat 4102 (butyltin tris(2-ethylhexanoate)) and 10 g of 1,6-hexanediol on the hot plate. . . Am. Chem. Soc., 1954, 76, 296 and Tetrahedron Lett., 1990, 413), 2.6 g of 1,6-hexanediol and 1.75 g of warm catalyst solution was placed in a 25 ml microware 1-neck rb (round bottom) flask connected to a distillation head and receiver. . .

DETD [0132] Preparation of catalyst: A catalyst solution was prepared by adding 0.039 g of Ni(COD).sub.2 (0.14 mmol) to 0.397 g of polyesterl (0.42 mmol of bidentate). . .

DETD [0133] Hydrocyanation of butadiene: 74 μ l of the above catalyst solution (0.0019 mmol Ni) were added to 2 reaction vials fitted with septum caps. The vials were cooled to -20°. . .

DETD [0134] Isomerization of 2-methyl-3-butene nitrile (2M3BN): 82 μ l of the above catalyst solution (0.0021 mmol Ni) were added to 2 reaction vials fitted with septum caps. 130 μ l of a cold solution. . .

DETD [0135] Hydrocyanation of 3,4 Pentenenitrile (3,4 PN): 116 μ l of the above catalyst solution (0.0030 mmol Ni), and 13 μ l of a solution of ZnCl.sub.2 in 3PN (0.0067 mmol ZnCl.sub.2) were added to. . . . (21 mmol) N,N'-dimethyl-1,6-hexanediamine, 30 g deionized water, and 10.9 g (21 mmol) diphenyl 2,2'-dihydroxy-1,1'-binaphthalene-3,3'-dicarboxylate. The reactor contents were purged with nitrogen.

DETD [0153] Preparation of catalyst: 0.059 g of branched polymer 1 was weighed into each of 3 reaction vials equipped with septum caps. 200 μ l. . .

DETD [0154] Hydrocyanation of butadiene: One of the catalyst samples prepared above was cooled to -20° C. and 280 μ l of a solution of butadiene in toluene (0.925 mmol). . .

DETD . . . (2M3BN): 130 μ l of a cold solution containing 2M3BN and valeronitrile (0.930 mmol 2M3BN) were added to one of the catalyst samples prepared above. The vial was sealed and heated at 125° C. for 3.0 hours. The reaction mixture was then. . .

DETD [0156] Hydrocyanation of 3,4 Pentenenitrile (3,4 PN): One of the catalyst samples prepared above was cooled to -20° C. and 125 μ l of a solution of HCN, t-3PN, and 2-ethoxyethyl ether. . .

DETD [0158] Preparation of catalyst: 0.056 g of branched polymer 2 was weighed into each of 3 reaction vials equipped with septum caps. 200 μ l. . .

DETD [0159] Hydrocyanation of butadiene: One of the catalyst samples prepared above was cooled to -20° C. and 280 μ l of a solution of butadiene in toluene (0.925 mmol). . .

DETD . . . (2M3BN): 130 μ l of a cold solution containing 2M3BN and valeronitrile (0.930 mmol 2M3BN) were added to one of the catalyst samples prepared above. The vial was sealed and placed in a hot block reactor set at 125° C. The sample. . .

DETD [0161] Hydrocyanation of 3,4 Pentenenitrile (3,4 PN): One of that catalyst samples prepared above was cooled to -20° C. and 125 μ l of a solution of HCN, t-3PN, and 2-ethoxyethyl ether. . .

DETD . . . 1-8 and one of aromatic diol A--E. Examples 7-9 and 13-14 illustrate the importance of control of polymer morphology on catalyst activity and selectivity. ##STR11##

TABLE 1

Selectivity and activity of several catalysts comprising polymeric phosphite ligands in the hydrocyanation of butadiene and t-3 pentenenitrile, and the isomerization of 2-methyl-3-butene nitrile
3PN hydrocyanation
BD hydrocyanation. . .

CLM What is claimed is:
42. A process comprising an unsaturated compound with a fluid comprising hydrogen cyanide in the presence of a catalyst composition recited in any of claims 18 to 21.

45. A process comprising (a) contacting a diolefinic compound, in the presence of a catalyst composition, with a fluid comprising hydrogen cyanide to produce a 2-alkyl-3-monoalkenenitrile; and (b) contacting said 2-alkyl-3-monoalkenenitrile with said catalyst composition wherein said catalyst composition is recited in claims 18-21.

48. A process comprising contacting a 2-alkyl-3-monoalkenenitrile with a catalyst composition recited in claims 18-21.

IT 4635-87-4P, 3-Pentenenitrile 16529-56-9P, 2-Methyl-3-butenenitrile
(polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)

IT 74-90-8, Hydrogen cyanide, reactions 592-51-8, 4-Pentenenitrile 818-57-5, Methyl 4-pentenoate 818-58-6, Methyl 3-pentenoate 818-59-7, Methyl 2-pentenoate

(polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)

PI US 2001049431 A1 20011206 <--!
US 6855799 B2 20050215

AB A polymeric composition, a process for producing the composition, and a process for using the composition in, for example, hydrocyanation or isomerization are disclosed. The composition comprises repeat units derived from (1) a carbonyl compound, a monomer, and phosphorochloridite; (2) phosphorus trichloride, a polyhydric alcohol, and an aromatic diol; or (3) combinations of (1) and (2) in which the monomer can be a polyhydric alcohol, an amine, combinations thereof. The composition can further comprise a Group VIII metal and optionally a Lewis acid. The composition can be produced by (1) contacting a carbonyl compound with the monomer to produce an intermediate and contacting the intermediate with phosphorochloridite; (2) contacting phosphorus trichloride with a second polyhydric alcohol under a condition sufficient to produce a phosphorus-containing polymer and contacting the phosphorus-containing polymer with an aromatic diol; or (3) contacting an N,N-dialkyl dichlorophosphoramidite with a second polyhydric alcohol to produce a polymer phosphoramidite, contacting the polymer phosphoramidite with an acid such as HCl to produce the phosphorus-containing polymer, which is then contacted with an aromatic diol. The composition can be used as catalyst, for example, for converting an unsaturated organic compound to a nitrile and isomerizing a nitrile.

SUMM [0001] This invention relates to a polymeric phosphite composition and polymeric phosphite catalyst composition that can be useful for a variety of catalytic processes, to a process for producing the composition, and to a process for using the composition in the hydrocyanation of unsaturated organic compounds and the isomerization of unsaturated nitriles.

SUMM [0002] Phosphorus-based ligands are ubiquitous in catalysis, finding use for a number of commercially important chemical transformations. Phosphorus-based ligands commonly encountered in catalysis include phosphines and phosphites. Monophosphine and monophosphite ligands are compounds which contain a single phosphorus atom which serves as a donor to a transition metal. Bisphosphine, bisphosphite, and bis(phosphorus) ligands in general, contain two phosphorus donor atoms and typically form cyclic chelate structures with transition metals.

SUMM [0003] Two industrially important catalytic reactions using phosphorus ligands of particular importance are olefin hydrocyanation and isomerization of branched nitriles to linear nitriles. Phosphite ligands are particularly good ligands for both reactions. The hydrocyanation of

ethylenically unsaturated compounds using transition metal complexes with monodentate phosphite ligands is well documented in the prior art. See for example U.S. Pat. Nos. 3,496,215; 3,631,191; 3655,723; 3,766,237; and 5,543,536. Bidentate phosphite ligands have also been shown to be particularly useful ligands in the hydrocyanation of activated ethylenically unsaturated compounds. See for example, Baker, M. J., and Pringle, P. G., J. Chem. Soc., Chem. Commun., 1292, 1991; Baker et al., J. Chem. Soc., Chem. Commun., 803, 1991; WO 93,03839; U.S. Pat. Nos. 5,512,696; 5,723,641; 5,688,986.

- SUMM [0004] Recovery of the ligand and catalyst is important for a successful process. Typical separation procedures to remove the product(s) from the catalyst and ligand involve extraction with an immiscible solvent or distillation. It is usually difficult to recover the catalyst and ligand quantitatively. For instance, distillation of a volatile product from a non-volatile catalyst results in thermal degradation of the catalyst. Similarly, extraction results in some loss of catalyst into the product phase. For extraction, one would like to be able to tune the solubility of the ligand and catalyst to disfavor solubility in the product phase. These ligands and metals are often very expensive and thus it is important to keep such losses to a minimum for a commercially viable process.
- SUMM [0005] One method to solve the problem of catalyst and product separation is to attach the catalyst to an insoluble support. Examples of this approach have been previously described, and general references on this subject can be found in "Supported Metal Complexes", D. Reidel Publishing, 1985, Acta Polymer., 1996, 47, 1; Comprehensive Organometallic Chemistry, Pergamon Press, 1982, Chapter 55; and Beller, M., Cornils, B., Frohning, C. D., Kohlpaintner, C. W., Journal of Molecular Catalysis A, 104, 1995, 17-85 and Macromol. Symp. 1994, 80, 241. Specifically, monophosphine and monophosphite ligands attached to solid supports are described in these references. Bisphospine ligands have also been attached to solid supports and used for catalysis, as described in for example U.S. Pat. No. 5,432,289; J. Mol. Catal. A, 1996, 112,217; and J. Chem. Soc., Chem. Commun., 1996, 653. The solid support in these prior art examples can be organic, e.g., a polymer resin, or inorganic in nature.
- SUMM [0007] There is always a need to develop a composition that can be used as or in a catalyst with substantially reduced loss during a catalytic reaction or separation of product from the catalyst. An object of the present invention is, therefore, to provide such a composition and to provide processes for making and for using the composition.
- SUMM [0008] An advantage of the invention composition is that varying the molecular weight and degree of branching can control the solubility of the composition. Another advantage of the invention is that the catalyst produced by the composition can be substantially recovered by filtration. Other objects and advantages of the present invention will become apparent as the invention is more fully disclosed below.
- SUMM [0010] According to a second embodiment of the invention, a composition that can be used as a catalyst is provided, which comprises (1) composition disclosed in the first embodiment, (2) a Group VIII metal selected from Ni, Co, Pd, and combinations of two or more thereof, and optionally (3) a Lewis acid.
- SUMM [0014] According to a sixth embodiment of the invention, a process is

provided. The process comprises contacting, in the presence of a catalyst disclosed in the second embodiment of the invention, an unsaturated organic compound with a hydrogen cyanide-containing fluid under a condition sufficient to produce a nitrile.

SUMM [0015] According to a seventh embodiment of the invention, a process is provided. The process comprises contacting a nitrile with the catalyst disclosed in the second embodiment of the invention to produce linear 3-alkenenitrile.

SUMM [0054] These polyhydric alcohols can be produced by those skilled in the art. For example, the diacetal can be prepared by refluxing di(trimethylolpropane) with salicylaldehyde with oxalic acid as catalyst. For references for preparing acetal from acid catalyzed reaction of an aldehyde and an alcohol, see Tetrahedron, 1996, 14599; Tet. Lett., 1989, 1609; Tetrahedron, 1990, 3315. 1,3-bis(2-hydroxyphenoxy)propane was prepared by a literature procedure, J. Org. Chem., 48, 1983, 4867. 4,4'-ethylidenebis(2,5-dimethylphenol); 4,4'-propylidenebis(2,5-dimethylphenol); 4,4'-benzylidenebis(2,5-dimethylphenol); and 4,4'-ethylidenebis(2-isopropyl-5-methylphenol) can be prepared according to Bull. Chem. Soc. Jpn., 62, 3603 (1989).

SUMM [0065] The solubilities of these composition or polymeric phosphite ligands disclosed above generally depend on the molecular weight of the polymer and degree of branching. For soluble polymeric system, separation can therefore be done by extraction. With insoluble polymeric systems, the catalyst can be placed in fixed beds or separated by filtration from a reaction mixture. Alternatively, the solubility of the polymer can be adjusted to be soluble in the reactants and insoluble in the products. Thus, the reaction can be carried out homogeneously to obtain high conversion. The polymeric catalyst can then be separated by easy means such as decantation or filtration.

SUMM [0066] According to the second embodiment of the invention, the compositions disclosed above can be combined with a Group VIII metal and, optionally, a Lewis acid to produce a catalyst composition. The term "Group VIII" refers to the ACS version of the Periodic Table of the Elements, 67.sup.th edition (1986-1987), CRC Handbook of Chemistry and Physics, Press, Boca Raton, Fla. The term "Group VIII metal" used in the invention can also refer to Group VIII metal compound or Group VIII metal complex.

SUMM [0067] Generally, a Group VIII compound is combined with a polymer disclosed above to produce a desired catalyst. Among the Group VIII compounds, a nickel compound, a cobalt compound, or a palladium compound is preferred. A nickel compound is more preferred. A zero-valent nickel compound containing a ligand that can be displaced by the polymer is the most preferred source of Group VIII metal. Zero-valent nickel compounds can be prepared or generated according to means known in the art such as disclosed in U.S. Pat. Nos. 3,496,217; 3,631,191; 3,846,461; 3,847,959 and 3,903,120. Two such preferred zero-valent nickel compounds are Ni(COD).sub.2 (COD is 1,5-cyclooctadiene) and Ni{P(O---O---C.sub.6H.sub.4CH.sub.2).sub.2} (C.sub.6H.sub.4CH.sub.2 is 1,4-phenylene), both of which are known in the art.

SUMM [0068] Alternatively, divalent nickel compounds can be combined with a reducing agent, to serve as a source of zero-valent nickel in the reaction. Suitable divalent nickel compounds include compounds of the formula NiY.sub.2 where Y is halide, carboxylate, or acetylacetone. Suitable reducing agents include metal borohydrides, metal aluminum

hydrides, metal alkyls, Li, Na, K, or H.₂. Elemental nickel, preferably nickel powder, when combined with a halogenated catalyst, as described in U.S. Pat. No. 3,903,120, is also a suitable source of zero-valent nickel.

SUMM [0069] The amount of transition metal can be any amount so long as favorable results can be obtained with respect to catalyst activity and process economy, when used as a catalyst. In general, the molar ratio of phosphorus ligand to transition metal generally can be from about 1:1 to about 100:1, preferably from about 1:1 to about 20:1 (moles phosphorus per mole metal).

SUMM [0071] The composition of the second embodiment of the invention can further comprise one or more Lewis acid promoters that affect both the activity and the selectivity of the catalyst system. The promoter can be an inorganic or organometallic compound in which the promoter contains at least one element selected from scandium, titanium, vanadium, chromium, manganese, iron, cobalt, copper, zinc, boron, aluminum, yttrium, zirconium, niobium, molybdenum, cadmium, rhenium and tin. Examples include ZnBr₂, ZnI₂, ZnCl₂, ZnSO₄, CuCl₂, Cu₂, Cu(O₂)₃SCF₃, CoCl₂, CoI₂, FeI₂, FeCl₂, FeCl₃, FeCl₂(THF), FeCl₂, TiCl₄, TiCl₃, ClTi(O*i*Pr)₂, MnCl₂, ScCl₃, AlCl₃, (C₂H₅)₂AlCl₂, (iso-C₂H₅)₂AlCl₂, Ph₂AlCl, PhAlCl₂, ReCl₅, ZrCl₄, NbCl₅, VCl₃, CrCl₃, MoCl₅, YCl₃, CdCl₂, LaCl₃, Er(O₂)₃SCF₃, Yb(O₂)₂CCF₃, SmCl₃, B(C₂H₅)₂AlCl₂, TaCl₅. Suitable promoters are further described in U.S. Pat. Nos. 3,496,217; 3,496,218 and 4,774,353. These include metal salts (such as ZnCl₂, CoI₂, and SnCl₂), and organometallic compounds (such as RAlCl₂, R₂SnCl₃SCF₃, and R₂B, where R is an alkyl or aryl group). U.S. Pat. No. 4,874,884 describes how synergistic combinations of promoters can be chosen to increase the catalytic activity of the catalyst system. Preferred promoters include CdCl₂, FeCl₂, ZnCl₂, B(C₂H₅)₂AlCl₂, and (C₂H₅)₂AlCl₂, where X=CF₃, SO₃⁻, CH₂=CH₂, or (C₂H₅)₂BCN. The mole ratio of promoter to Group VIII metal can be in the range of from about 1:1 to about 1000:1, preferably about 1:16 to about 50:1.

SUMM [0093] According to the sixth embodiment of the invention, a process that can be used in organic compound conversions is provided. The process can comprise, consist essentially of, or consist of contacting, in the presence of a catalyst composition, an unsaturated organic compound with a hydrogen cyanide-containing fluid under a condition sufficient to produce a nitrile wherein the catalyst composition can be the same as that disclosed in the second embodiment of the invention. The term "fluid" can be gas, liquid, or both. Any fluid containing about 1 to 100% HCN can be used.

SUMM [0097] The unsaturated organic compound can also be substituted with one or more functional groups containing a heteroatom, such as oxygen, sulfur, nitrogen or phosphorus. Examples of these heteroatom-substituted ethylenically unsaturated organic compounds include vinyl methyl ether, methyl oleate, oleyl alcohol, 3-pentenenitrile, 4-pentenenitrile, 3-pentenoic acid, 4-pentenoic acid, methyl 3-pentenoate, acrylonitrile, acrylic acid esters, methyl acrylate, methacrylic acid esters, methyl methacrylate, acrolein, allyl alcohol

and combinations of two or more thereof.

SUMM [0098] The hydrocyanation process can be carried out, for example, by charging a suitable vessel such as a reactor with an unsaturated compound, catalyst composition, and solvent, if any to form a reaction mixture. Hydrogen cyanide can be initially combined with other components to form the mixture. However, it is preferred that HCN is added slowly to the mixture after other components have been combined. Hydrogen cyanide can be delivered as a liquid or as a vapor to the reaction. As an alternative, a cyanohydrin can be used as the source of HCN. See, for example, U.S. Pat. No. 3,655,723.

SUMM [0099] Another suitable technique is to charge the vessel with the catalyst and the solvent to be used, and feed both the unsaturated compound and the HCN slowly to the reaction mixture.

SUMM [0100] The molar ratio of unsaturated compound to catalyst can be varied from about 10:1 to about 10000:1. The molar ratio of HCN to catalyst generally is varied from about 10:1 to 100,000:1, preferably 100:1 to 5,000:1, for a batch operation. In a continuous operation, such as when using a fixed bed catalyst type of operation, a higher proportion of catalyst can be used such as 5:1 to 100,000:1, preferably 100:1 to 5,000:1, HCN to catalyst.

SUMM [0102] The hydrocyanation can be carried out with or without a solvent. The solvent, if used, can be liquid at the reaction temperature and pressure and inert towards the unsaturated compound and the catalyst. Suitable solvents include hydrocarbons such as benzene, xylene, or combinations thereof; ethers such as tetrahydrofuran (THF); nitriles such as acetonitrile, benzonitrile, adiponitrile, or combinations of two or more thereof. The unsaturated compound to be hydrocyanated can itself serve as the solvent. Hydrocyanation can also be carried out in gas phase.

SUMM [0103] The exact temperature is dependent to a certain extent on the particular catalyst being used, the particular unsaturated compound being used and the desired rate. Normally, temperatures of from -25° C. to 200° C. can be used, the range of 0° C. to 150° C. being preferred.

SUMM [0109] Examples of the unsaturated compounds include, but are not limited to, unsaturated organic compounds containing from 2 to approximately 30 carbon atoms. 3-Pentenenitrile and 4-pentenenitrile are especially preferred. When nonconjugated acyclic aliphatic monoethylenically unsaturated compounds are used, up to about 10% by weight of the monoethylenically unsaturated compound can be present in the form of a conjugated isomer, which itself may undergo hydrocyanation. For example, when 3-pentenenitrile is used, as much as 10% by weight thereof may be 2-pentenenitrile. (As used herein, the term "pentenenitrile" is intended to be identical with "cyanobutene"). Suitable unsaturated compounds include unsubstituted hydrocarbons as well as hydrocarbons substituted with groups, which do not attack the catalyst, such as cyano. These unsaturated compounds include, but are not limited to, monoethylenically unsaturated compounds containing from 2 to 30 carbons such as ethylene, propylene, butene-1, pentene-2, hexene-2, and combinations of two or more thereof; nonconjugated diethylenically unsaturated compounds such as allene, substituted compounds such as 3-pentenenitrile, 4-pentenenitrile, methyl pent-3-enoate, and combinations of two or more thereof; and ethylenically unsaturated compounds having perfluoroalkyl substituents such as, for

example, C._{sub.z}F._{sub.2z+1}, where z is an integer of up to 20. The monoethylenically unsaturated compounds can also be conjugated to an ester group such as methyl pent-2-enoate.

- SUMM [0112] The process of the invention can be carried out in the presence of one or more Lewis acid promoters that affect both the activity and the selectivity of the catalyst system. The promoter is the same as that disclosed above.
- SUMM [0119] For example, 2-alkyl-3-monoalkenenenitrile used as the starting material in the isomerization of the invention can result from the hydrocyanation of a diolefin disclosed above or can come from any other available sources. The olefinic double bond in the 2-alkyl-3-monoalkenenenitriles used as the starting materials in the isomerization of this invention cannot be conjugated to the triple bond of the cyano group. Suitable starting 2-alkyl-3-monoalkenenenitriles can also carry groups that do not attack the catalyst, for example, another cyano group. Preferably, the starting 2-alkyl-3-monoalkenenenitriles contain from 5 to 8 carbon atoms, excluding any additional substitution. 2-Methyl-3-butenenitrile is especially important in the production of adiponitrile. Other representative nitriles include 2-ethyl-3-butenenitrile and 2-propyl-3-butenenitrile.
- SUMM [0122] The process can be carried out in the absence or in the presence of a solvent or diluent. Any solvent or diluent that is inert to or nondestructive of the catalyst can be used, however. Suitable solvents include, but are not limited to, aliphatic or aromatic hydrocarbons (hexane, cyclohexane, benzene), ethers (diethyl ether, tetrahydrofuran, dioxane, glycol dimethyl ether, anisole), esters (ethyl acetate, methyl benzoate, THF), nitrites (acetonitrile, benzonitrile), or combinations of two or more thereof.
- SUMM [0123] A nonoxidizing environment is desirable in order to retard oxidative deactivation of the catalyst. Accordingly, an inert atmosphere, e.g., nitrogen, is preferably used, although air can be used if desired at the expense of loss of a proportion of the catalyst through oxidation.
- SUMM [0124] The nickel complex is essentially nonvolatile, whereas the 2-methyl-3-butenenitrile reactant and the linear pentenenitrile products are relatively volatile. Accordingly, in a continuous flow procedure, the catalyst can be a component of the flowing system in a completely liquid-phase operation. It can also be in a mobile non-flowing liquid state in a semi-vapor phase operation, or it may be in a fixed-bed state in a conventional flowing vapor-phase operation.
- SUMM [0126] The molar ratio of 2-alkyl-3-monoalkenenenitrile to catalyst is generally greater than 1:1, usually in the range from about 5:1 to 20,000:1, preferably 100:1 to 5,000:1, for a batch or continuous operation.
- DET_D [0127] The following non-limiting, representative examples illustrate the process and catalyst compositions of this invention. All parts, proportions, and percentages are by weight, unless otherwise indicated. In each example, the following procedure was used unless otherwise noted.
- DET_D [0129] A catalyst solution was prepared by warming 0.1 g Fascat 4102 (butyltin tris(2-ethylhexanoate)) and 10 g of 1,6-hexanediol on the hot plate in a small vial with a small magnet. The solution was kept warm. A mixture containing 5 g of dimethyl 2,2'-dihydroxy-1,1'-binaphthalene-

- 3,3'-dicarboxylate (0.0123 mmoles; reference for preparation; see J. Am. Chem. Soc., 1954, 76,296 and Tetrahedron Lett., 1990, 413), 2.6 g of 1,6-hexanediol and 1.75 g of warm catalyst solution was placed in a 25 ml microware 1-neck rb (round bottom) flask connected to a distillation head and receiver with a pre-calibrated heating mantle while stirring magnetically until methanol started to distill off (the temperature was about 180° C. at which temperature the dimethyl 2,2'-dihydroxy-1,1'-binaphthalene-3,3'-dicarboxylate had all dissolved). The temperature was then increased until the 1,6-hexanediol started to reflux in the top of the flask (220° C.). The mixture was allowed to reflux for about an hour and then house vacuum was gradually applied. Full pump vacuum was then applied to distill off the excess 1,6-hexanediol. The pressure was lowered very slowly to 4 mm Hg over the next two hours in order to avoid bumping. The reaction mixture was then polymerized at 270° C. for 2 hours while distilling off most of the 1,6-hexanediol. After cooling, the reaction mixture was refluxed with 25 ml of acetone for three hours and then cooled and filtered. NMR indicated degree of polymerization to be 6.
- DETD** [0132] Preparation of catalyst: A catalyst solution was prepared by adding 0.039 g of Ni(COD)₂ (0.14 mmol) to 0.397 g of polyesterl (0.42 mmol of bidentate phosphite equivalents; the unit formula weight of the polymers were determined based on the expected formula) in 4.568 g toluene.
- DETD** [0133] Hydrocyanation of butadiene: 74 µl of the above catalyst solution (0.0019 mmol Ni) were added to 2 reaction vials fitted with septum caps. The vials were cooled to -20° C. and 120 µl of a solution of HCN in valeronitrile (0.830 mmol HCN) and 280 µl of a solution of butadiene (BD) in toluene (0.925 mmol BD) were added to each vial. The vials were sealed and placed in a hot-block reactor set at 80° C. Samples were removed after 1.5 and 3 hours and quenched by cooling to -20° C. The reaction mixtures were then diluted in ethyl ether and the product distribution analyzed by GC against valeronitrile as an internal standard. Analysis showed that 67.5 and 68.7% of the starting HCN had been converted to useful pentenenitriles (the 3-pentenenitrile to 2-methyl-3-butenenitrile ratio was 1.1) after 1.5 and 3 hours respectively.
- DETD** [0134] Isomerization of 2-methyl-3-butene nitrile (2M3BN): 82 µl of the above catalyst solution (0.0021 mmol Ni) were added to 2 reaction vials fitted with septum caps. 130 µl of a cold solution containing 2M3BN and valeronitrile (0.930 mmol 2M3BN) were added to each vial. The vials were sealed and placed in a hot block reactor set at 125° C. Samples were removed after 1.5 and 3.0 hrs, cooled and diluted in ethyl ether. The product distribution was analyzed by GC using valeronitrile as an internal standard. The 3PN/2M3BN ratio was 3.88 after 1.5 hrs and 5.50 after 3 hours.
- DETD** [0135] Hydrocyanation of 3,4 Pentenenitrile (3,4 PN): 116 µl of the above catalyst solution (0.0030 mmol Ni), and 13 µl of a solution of ZnCl₂ in 3PN (0.0067 mmol ZnCl₂) were added to a vial fitted with a septum cap. The vial was cooled to -20° C. and 125 µl of a solution of HCN, t-3PN, and 2-ethoxyethyl ether (0.396 mmol HCN, 0.99 mmol t-3PN) was added. The vial was sealed and set aside for 24 hours at room temperature. The reaction mixture was diluted with ethyl ether and the product distribution analyzed by GC using 2-ethoxyethyl ether as an internal standard. Analysis showed that 35.3% of the starting pentenenitriles had been converted to dinitrile product (88.1% yield based on HCN.) The selectivity to the linear ADN isomer was 92.7%.
- DETD** [0142] 1. A 75-cc stainless steel autoclave equipped with a glass sleeve

- was charged with 3.05 g (21 mmol) N,N'-dimethyl-1,6-hexanediamine, 30 g deionized water, and 10.9 g (21 mmol) diphenyl 2,2'-dihydroxy-1,1'-binaphthalene-3,3'-dicarboxylate. The reactor contents were purged with nitrogen.
- DETD [0153] Preparation of catalyst: 0.059 g of branched polymer 1 was weighed into each of 3 reaction vials equipped with septum caps. 200 μ l of THF were added to each vial and the sample shaken. 320 μ l of a freshly made solution containing 0.015 mmol Ni(COD).sub.2 in toluene were added to each vial.
- DETD [0154] Hydrocyanation of butadiene: One of the catalyst samples prepared above was cooled to -20° C. and 280 μ l of a solution of butadiene in toluene (0.925 mmol BD) and 120 μ L of a solution of HCN in valeronitrile (0.830 mmol HCN) were added to the vial. The vial was sealed and heated at 80° C. for 3 hours. After a quench by cooling to -20° C., the reaction mixture was then diluted in ethylether and the product distribution analyzed by GC against valeronitrile as an internal standard. Analysis showed that 71.7% of the starting HCN had been converted to useful pentenenitriles (ratio of 3PN/2M3BN was 1.36) after 3 hours.
- DETD [0155] Isomerization of 2-methyl-3-butene nitrile (2M3BN): 130 μ l of a cold solution containing 2M3BN and valeronitrile (0.930 mmol 2M3BN) were added to one of the catalyst samples prepared above. The vial was sealed and heated at 125° C. for 3.0 hours. The reaction mixture was then cooled and diluted in ethyl ether. The product distribution was analyzed by GC using valeronitrile as an internal standard. The 3PN/2M3BN ratio was 0.47 after 3 hrs.
- DETD [0156] Hydrocyanation of 3,4 Pentenenitrile (3,4 PN): One of the catalyst samples prepared above was cooled to -20° C. and 125 μ l of a solution of HCN, t-3PN, and 2-ethoxyethyl ether (0.396 mmol HCN, 0.99 mmol t-3PN) was added. 13 μ l of a solution of ZnCl.sub.2 in 3PN (0.0067 mmol ZnCl.sub.2) were added to the vial. The vial was sealed and set aside for 24 hours at room temperature. The reaction mixture was diluted with ethyl ether and the product distribution analyzed by GC using 2-ethoxyethyl ether as an internal standard. Analysis showed that 23.4% of the starting pentenenitriles had been converted to dinitrile product (64.6% yield based on HCN.) The selectivity to the linear ADN isomer was 91.8%.
- DETD [0158] Preparation of catalyst: 0.056 g of branched polymer 2 was weighed into each of 3 reaction vials equipped with septum caps. 200 μ l of THF were added to each vial and the sample shaken. 320 μ l of a freshly made solution of 39 mg Ni(COD).sub.2 in 2.79 g toluene (0.015 mmol Ni) were added to each vial.
- DETD [0159] Hydrocyanation of butadiene: One of the catalyst samples prepared above was cooled to -20° C. and 280 μ l of a solution of butadiene in toluene (0.925 mmol BD) and 120 μ l of a solution of HCN in valeronitrile (0.830 mmol HCN) were added to the vial. The vial was sealed and placed in a hot-block reactor set at 80° C. The sample was removed after 3 hours and quenched by cooling to -20° C. The reaction mixture was then diluted in ethylether and the product distribution analyzed by GC against valeronitrile as an internal standard. Analysis showed that 84.8% of the starting HCN had been converted to useful pentenenitriles (ratio of 3PN/2M3BN was 0.51) after 3 hours.
- DETD [0160] Isomerization of 2-methyl-3-butene nitrile (2M3BN): 130 μ l of a cold solution containing 2M3BN and valeronitrile (0.930 mmol 2M3BN) were added to one of the catalyst samples prepared above. The vial was sealed and placed in a hot block reactor set at 125° C. The sample was removed after 3.0 hours, cooled and diluted in ethyl ether.

The product distribution was analyzed by GC using valeronitrile as an internal standard. The 3PN/2M3BN ratio was 0.8 after 3 hrs.

DETD [0161] Hydrocyanation of 3,4 Pentenenitrile (3,4 PN): One of that catalyst samples prepared above was cooled to -20° C. and 125 µl of a solution of HCN, t-3PN, and 2-ethoxyethyl ether (0.396 mmol HCN, 0.99 mmol t-3PN) was added. 13 µl of a solution of ZnCl₂.sub.2 in 3PN (0.0067 mmol ZnCl₂.sub.2) were added to the vial. The vial was sealed and set aside for 24 hours at room temperature. The reaction mixture was diluted with ethyl ether and the product distribution analyzed by GC using 2-ethoxyethyl ether as an internal standard. Analysis showed that 1.8% of the starting pentenenitriles had been converted to dinitrile product (5.0% yield based on HCN). The selectivity to the linear ADN isomer was 90.0%.

DETD [0168] In the representative examples in Table 1 the polymeric phosphite was prepared from one of the polyhydric alcohol 1-8 and one of aromatic diol A-E. Examples 7-9 and 13-14 illustrate the importance of control of polymer morphology on catalyst activity and selectivity.

#STR11#

TABLE 1

Selectivity and activity of several catalysts comprising polymeric phosphite ligands in the hydrocyanation of butadiene and t-3 pentenenitrile, and the isomerization of 2-methyl-3-butenenitrile

| Example | Isomerization 3PN/2M3BN | diol | bridge | BD hydrocyanation | | 3PN hydrocyanation | | Selectivity to ADN |
|-------------------|----------------------------|------|--------|-------------------|---------|--------------------|---------|-----------------------|
| | | | | yield.sup.a) | 3PN/2M3 | yield.sup.a) | 3PN/2M3 | |
| 7.sup.b, 11.66 | 1 | A | | 29.5 | 0.9 | 66.5 | 88.8 | |
| 8.sup.c, 11.69 | 1 | A | | 76.9 | 1.9 | 59.0 | 88.6 | |
| 9.sup.c, 26.39 | 1 | A | | 77.1 | 8.2 | 63.0 | 89.7 | |
| 10.sup.c) | 1 | B | | 32.0 | 0.7 | 50.2 | 80.7 | 5.28 |
| 11.sup.c) | 1 | D | | 68.2 | 1.5 | 50.8 | 87.1 | 17.17 |
| 12.sup.c, 1.57 | 1 | B | | 74.0 | 0.8 | 49.5 | 83.6 | |
| 13.sup.c, 2.82 | 1 | E | | 70.1 | 1.0 | 67.0 | 88.4 | |
| 14.sup.c) | 2 | C | | 83.5 | 1.2 | 43.5 | 78.7 | 17.81 |
| 15.sup.c) | 3 | A | | 69.9 | 31.5 | 59.5 | 92.8 | 21.01 |
| 16.sup.c) | 5 | C | | 74.4 | 18.2 | 62.5 | 90.1 | 21.93 |
| 17.sup.c) | 4 | A | | 73.8 | 2.5 | 38.5 | 94.4 | 1.51 |
| 18.sup.c) | 6 | A | | 73.6 | 19.5 | 63.3 | 91.9 | 18.72 |
| 19.sup.c) | 7 | A | | 86.0 | 2.7 | 50.8 | 95.5 | 15.47 |
| 20.sup.c) | 7 | C | | 86.5 | 1.3 | 12.0 | 94.7 | 16.81 |
| 21.sup.c) | 8 | D | | 84.5 | 2.5 | 31.25 | 89.9 | 18.28 |

.sup.a)Yield in % based on HCN.

.sup.b)Hydrocyanation and isomerization procedure analogous to that in Example 1A.

.sup.c)Hydrocyanation and isomerization procedure analogous to that in Example 4A.

.sup.d)770 mg 1 were added to 412 mg PCl₂.sub.3 in a mixture of 30 ml toluene and 20 ml THF at -30° C. 800 mg NET₂.sub.3 in 20 ml toluene at -30° C. were added. Stirred 60 hrs. Added 363 mg A and 700 mg

NET.sub.3 in 10 ml THF. Product was isolated by filtration.

.sup.e) 650 mg NET.sub.3 in 5 ml THF were added to 412 mg PC1.sub.3 and 769 mg 1 in 15 ml THF at -30° C. over a period of 10 minutes. 3 ml THF were added and the slurry cooled in a -30° C. freezer. 363 mg A and 650 mg NET.sub.3 were added, resulting in a gel. 15 ml THF were added and the solution filtered. Solids were washed with hot H.sub.20, then with acetone, CH.sub.3CN and THF.

.sup.f) 650 mg NET.sub.3 in 15 ml THF were cooled to -30° C. and added to 412 mg PC1.sub.3 and 769 mg 1 in 20 ml of THF at -30° C.. The slurry was cooled after the addition. 363 mg A and 650 mg NET.sub.3 were added. The solution was filtered and solids washed with THF. The polymer was THF soluble.

.sup.g) 412 mg PC1.sub.3 and 769 mg 1 in 20 ml toluene and 20 ml THF were cooled to -30° C. in a freezer. 800 mg NET.sub.3 in 20 ml toluene were added and the mixture cooled to -30° C. 790 mg E and 700 mg NET.sub.3 were added. The mixture was filtered, washed with THF and the product recovered by removal of the solvent.

.sup.h) 1.679 g 1 was dissolved in 17 g toluene. 900 mg of PC1.sub.3 were added. 5 g N(nBu).sub.3 in 8.7 g toluene were cooled to -30° C. and added to the mixture. 1.727 g E, 2.6 g N(nBu).sub.3, and 20 ml toluene were added and the mixture stirred. The product was isolated by addition of CH.sub.3CN, filtration and washing with CH.sub.3CN.
42. A process comprising an unsaturated compound with a fluid comprising hydrogen cyanide in the presence of a catalyst composition recited in any of claims 18 to 21.

45. A process comprising (a) contacting a diolefinic compound, in the presence of a catalyst composition, with a fluid comprising hydrogen cyanide to produce a 2-alkyl-3-monoalkenenitrile; and (b) contacting said 2-alkyl-3-monoalkenenitrile with said catalyst composition wherein said catalyst composition is recited in claims 18-21.

48. A process comprising contacting a 2-alkyl-3-monoalkenenitrile with a catalyst composition recited in claims 18-21.

IT 4635-87-4P, 3-Pentenenitrile 16529-56-9P, 2-Methyl-3-butenenitrile

(polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)

IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,
Butadiene, reactions 592-51-8, 4-Pentenenitrile 818-57-5, Methyl 4-pentenoate 818-58-6, Methyl 3-pentenoate 818-59-7, Methyl 2-pentenoate

(polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)

IT 4635-87-4P, 3-Pentenenitrile
(polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)

RN 4635-87-4 USPATFULL

CN 3-Pentenenitrile (CA INDEX NAME)



IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,
Butadiene, reactions

(polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)

RN 74-90-8 USPATFULL

CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 USPATFULL

CN 1,3-Butadiene (CA INDEX NAME)



L88 ANSWER 56 OF 60 USPATFULL on STN

ACCESSION . . .

HCl to produce the phosphorus-containing polymer, which is then contacted with an aromatic diol. The composition can be used as catalyst, for example, for converting an unsaturated organic compound to a nitrile and isomerizing a nitrile.

CAS INDEXING IS AVAILABLE FOR. . .

AB . . . HCl to produce the phosphorus-containing polymer, which is then contacted with an aromatic diol. The composition can be used as catalyst, for example, for converting an unsaturated organic compound to a nitrile and isomerizing a nitrile.

SUMM This invention relates to a polymeric phosphite composition and polymeric phosphite catalyst composition that can be useful for a variety of catalytic processes, to a process for producing the composition, and to a process for using the composition in the hydrocyanation of. . .

SUMM Phosphorus-based ligands are ubiquitous in catalysis, finding use for a number of commercially important chemical transformations. Phosphorus-based ligands commonly encountered in catalysis include phosphines and phosphites. Monophosphine and monophosphite ligands are compounds which contain a single phosphorus atom which serves as a. . .

SUMM Two industrially important catalytic reactions using phosphorus ligands of particular importance are olefin hydrocyanation and isomerization of branched nitrates to linear nitrates. Phosphite ligands. . .

SUMM Recovery of the ligand and catalyst is important for a successful process. Typical separation procedures to remove the product(s) from the catalyst and ligand involve extraction with an immiscible solvent or distillation. It is usually difficult to recover the catalyst and ligand quantitatively. For instance, distillation of a volatile product from a non-volatile catalyst results in thermal degradation of the catalyst. Similarly, extraction results in some loss of catalyst into the product phase. For extraction, one would like to be able to tune the solubility of the ligand and catalyst to disfavor solubility in the product phase. These ligands and metals are often very expensive and thus it is important. . .

SUMM One method to solve the problem of catalyst and product separation is

to attach the catalyst to an insoluble support. Examples of this approach have been previously described, and general references on this subject can be . . . Chemistry, Pergamon Press, 1982, Chapter 55; and Beller, M., Cornils, B., Frohning, C. D., Kohlpaintner, C. W., Journal of Molecular Catalysis A, 104, 1995, 17-85 and Macromol. Symp. 1994, 80, 241. Specifically, monophosphine and monophosphite ligands attached to solid supports are described in these references. Bisphospine ligands have also been attached to solid supports and used for catalysis, as described in for example U.S. Pat. No. 5,432,289; J. Mol. Catal. A, 1996, 112,217; and J. Chem. Soc., Chem.. . .

SUMM There is always a need to develop a composition that can be used as or in a catalyst with substantially reduced loss during a catalytic reaction or separation of product from the catalyst. An object of the present invention is, therefore, to provide such a composition and to provide processes for making and. . .

SUMM . . . weight and degree of branching can control the solubility of the composition. Another advantage of the invention is that the catalyst produced by the composition can be substantially recovered by filtration. Other objects and advantages of the present invention will become. . .

SUMM According to a second embodiment of the invention, a composition that can be used as a catalyst is provided, which comprises (1) composition disclosed in the first embodiment, (2) a Group VIII metal selected from Ni, Co,. . .

SUMM . . . to a sixth embodiment of the invention, a process is provided. The process comprises contacting, in the presence of a catalyst disclosed in the second embodiment of the invention, an unsaturated organic compound with a hydrogen cyanide-containing fluid under a condition. . .

SUMM According to a seventh embodiment of the invention, a process is provided. The process comprises contacting a nitrile with the catalyst disclosed in the second embodiment of the invention to produce linear 3-alkenenitrile.

SUMM . . . skilled in the art. For example, the diacetal can be prepared by refluxing di(trimethylolpropane) with salicylaldehyde with oxalic acid as catalyst. For references for preparing acetal from acid catalyzed reaction of an aldehyde and an alcohol, see Tetrahedron, 1996, 14599; Tet. Lett., 1989, 1609; Tetrahedron, 1990,3315. 1,3-bis(2-hydroxyphenoxy)propane was prepared. . .

SUMM . . . and degree of branching. For soluble polymeric system, separation can therefore be done by extraction. With insoluble polymeric systems, the catalyst can be placed in fixed beds or separated by filtration from a reaction mixture. Alternatively, the solubility of the polymer. . . reactants and insoluble in the products. Thus, the reaction can be carried out homogeneously to obtain high conversion. The polymeric catalyst can then be separated by easy means such as decantation or filtration.

SUMM . . . the compositions disclosed above can be combined with a Group VIII metal and, optionally, a Lewis acid to produce a catalyst composition. The term "Group VIII" refers to the ACS version of the Periodic Table of the Elements, 67.sup.th edition (1986-1987),. . .

SUMM Generally, a Group VIII compound is combined with a polymer disclosed above to produce a desired catalyst. Among the Group VIII compounds, a nickel compound, a cobalt compound, or a palladium compound is preferred. A nickel compound. . .

SUMM . . . metal aluminum hydrides, metal alkyls, Li, Na, K, or H.sub.2. Elemental nickel, preferably nickel powder, when combined with a halogenated catalyst, as described in U.S. Pat. No. 3,903,120, is also a suitable source of zero-valent nickel.

SUMM The amount of transition metal can be any amount so long as favorable

results can be obtained with respect to catalyst activity and process economy, when used as a catalyst. In general, the molar ratio of phosphorus ligand to transition metal generally can be from about 1:1 to about 100:1. . . .

SUMM . . . invention can further comprise one or more Lewis acid promoters that affect both the activity and the selectivity of the catalyst system. The promoter can be an inorganic or organometallic compound in which the promoter contains at least one element selected. . . alkyl or aryl group). U.S. Pat. No. 4,874,884 describes how synergistic combinations of promoters can be chosen to increase the catalytic activity of the catalyst system. Preferred promoters include CdCl₂.sub.2, FeCl₂.sub.2, ZnCl₂.sub.2, B(C₂H₅).sub.5).sub.3, and (C₂H₅).sub.5 SnX, where X.dbd.CF₃.sub.3 SO₂.sub.3, CH₂.sub.3 C₂H₅.sub.5 SO₂.sub.3,

SUMM . . . compound conversions is provided. The process can comprise, consist essentially of, or consist of contacting, in the presence of a catalyst composition, an unsaturated organic compound with a hydrogen cyanide-containing fluid under a condition sufficient to produce a nitrile wherein the catalyst composition can be the same as that disclosed in the second embodiment of the invention. The term "fluid" can be. . . .

SUMM . . . unsaturated organic compound can also be substituted with one or more functional groups containing a heteroatom, such as oxygen, sulfur, nitrogen or phosphorus. Examples of these heteroatom-substituted ethylenically unsaturated organic compounds include vinyl methyl ether, methyl oleate, oleyl alcohol, 3-pentenenitrile, 4-pentenenitrile,

SUMM . . . process can be carried out, for example, by charging a suitable vessel such as a reactor with an unsaturated compound, catalyst composition, and solvent, if any to form a reaction mixture. Hydrogen cyanide can be initially combined with other components to. . . .

SUMM Another suitable technique is to charge the vessel with the catalyst and the solvent to be used, and feed both the unsaturated compound and the HCN slowly to the reaction mixture.

SUMM The molar ratio of unsaturated compound to catalyst can be varied from about 10:1 to about 10000:1. The molar ratio of HCN to catalyst generally is varied from about 10:1 to 100,000:1, preferably 100:1 to 5,000:1, for a batch operation. In a continuous operation, such as when using a fixed bed catalyst type of operation, a higher proportion of catalyst can be used such as 5:1 to 100,000:1, preferably 100:1 to 5,000:1, HCN to catalyst.

SUMM . . . solvent, if used, can be liquid at the reaction temperature and pressure and inert towards the unsaturated compound and the catalyst. Suitable solvents include hydrocarbons such as benzene, xylene, or combinations thereof; ethers such as tetrahydrofuran (THF); nitrites such as acetonitrile,

SUMM The exact temperature is dependent to a certain extent on the particular catalyst being used, the particular unsaturated compound being used and the desired rate. Normally, temperatures of from -25° C. to 200°. . . .

SUMM . . . with "cyanobutene"). Suitable unsaturated compounds include unsubstituted hydrocarbons as well as hydrocarbons substituted with groups, which do not attack the catalyst, such as cyano. These unsaturated compounds include, but are not limited to, monoethylenically unsaturated compounds containing from 2 to 30. . . .

SUMM . . . in the presence of one or more Lewis acid promoters that affect both the activity and the selectivity of the catalyst system. The promoter is the same as that disclosed above.

SUMM . . . to the triple bond of the cyano group. Suitable starting 2-alkyl-3-monoalkenenitriles can also carry groups that do not attack

- the catalyst, for example, another cyano group. Preferably, the starting 2-alkyl-3-monoalkenenitriles contain from 5 to 8 carbon atoms, excluding any additional substitution.
- SUMM . . . in the presence of a solvent or diluent Any solvent or diluent that is inert to or nondestructive of the catalyst can be used, however. Suitable solvents include, but are not limited to, aliphatic or aromatic hydrocarbons (hexane, cyclohexane, benzene), ethers.
- SUMM A nonoxidizing environment is desirable in order to retard oxidative deactivation of the catalyst Accordingly, an inert atmosphere, e.g., nitrogen, is preferably used, although air can be used if desired at the expense of loss of a proportion of the catalyst through oxidation.
- SUMM . . . nonvolatile, whereas the 2-methyl-3-butenenitrile reactant and the linear pentenenitrile products are relatively volatile. Accordingly, in a continuous flow procedure, the catalyst can be a component of the flowing system in a completely liquid-phase operation. It can also be in a mobile. . .
- SUMM The molar ratio of 2-alkyl-3-monoalkenenitrile to catalyst is generally greater than 1:1, usually in the range from about 5:1 to 20,000:1, preferably 100:1 to 5,000:1, for a. . .
- DETD The following non-limiting, representative examples illustrate the process and catalyst compositions of this invention. All parts, proportions, and percentages are by weight, unless otherwise indicated. In each example, the following. . .
- DETD A catalyst solution was prepared by warming 0.1 g Fascat 4102 (butyltin tris(2-ethylhexanoate)) and 10 g of 1,6-hexanediol on the hot plate. . . J. Am. Chem. Soc., 1954, 76,296 and Tetrahedron Lett., 1990, 413), 2.6 g of 1,6-hexanediol and 1.75 g of warm catalyst solution was placed in a 25 ml microware 1-neck rb (round bottom) flask connected to a distillation head and receiver. . .
- DETD Preparation of catalyst: A catalyst solution was prepared by adding 0.039 g of Ni(COD)₂ (0.14 mmol) to 0.397 g of polyester 1 (0.42 mmol of bidentate phosphite). . .
- DETD Hydrocyanation of butadiene: 74 μ l of the above catalyst solution (0.0019 mmol Ni) were added to 2 reaction vials fitted with septum caps. The vials were cooled to -20°. . .
- DETD Isomerization of 2-methyl-3-butene nitrile (2M3BA): 82 μ l of the above catalyst solution (0.0021 mmol Ni) were added to 2 reaction vials fitted with septum caps. 130 μ l of a cold solution. . .
- DETD Hydrocyanation of 3,4 Pentenenitrile (3,4 PN): 116 μ l of the above catalyst solution (0.0030 mmol Ni), and 13 μ l of a solution of ZnCl₂.sub.2 in 3PN (0.0067 mmol ZnCl₂.sub.2) were added to. . .
- DETD . . . (21 mmol) N,N'-dimethyl-1,6-hexanediamine, 30 g deionized water, and 10.9 g (21 mmol) diphenyl 2,2'-dihydroxy-1,1'-binaphthalene-3,3'-dicarboxylate. The reactor contents were purged with nitrogen.
- DETD Preparation of catalyst: 0.059 g of branched polymer 1 was weighed into each of 3 reaction vials equipped with septun caps. 200 μ l. . .
- DETD Hydrocyanation of butadiene: One of the catalyst samples prepared above was cooled to -20° C. and 280 μ l of a solution of butadiene in toluene (0.925 mmol). . .
- DETD . . . (2M3BN): 130 μ l of a cold solution containing 2M3BN and valeronitrile (0.930 mmol 2M3BN) were added to one of the catalyst samples prepared above. The vial was sealed and heated at 125° C. for 3.0 hours. The reaction mixture was then. . .
- DETD Hydrocyanation of 3,4 Pentenenitrile (3,4 PN): One of the catalyst samples prepared above was cooled to -20° C. and 125 μ l of a solution of HCN, t-3PN, and 2-ethoxyethyl ether. . .
- DETD Preparation of catalyst: 0.056 g of branched polymer 2 was weighed

into each of 3 reaction vials equipped with septum caps. 200 μ l. . .

- DETD Hyarocyanation of butadiene: One of the catalyst samples prepared above was cooled to -20° C. and 280 μ l of a solution of butadiene in toluene (0.925 mmol). . .
- DETD . . . (2M3BN): 130 μ l of a cold solution containing 2M3BN and valeronitrile (0.930 mmol 2M3BN) were added to one of the catalyst samples prepared above. The vial was sealed and placed in a hot block reactor set at 125° C. The sample. . .
- DETD Hydrocyanation of 3,4 Pentenenitrile (3,4 PN): One of that catalyst samples prepared above was cooled to -20° C. and 125 μ l of a solution of HCN, t-3PN, and 2-ethoxyethyl ether. . .
- DETD . . . 1-8 and one of aromatic diol A-E. Examples 7-9 and 13-14 illustrate the importance of control of polymer morphology on catalyst activity and selectivity.

DETD TABLE 1

Selectivity and activity of several catalysts comprising polymeric phosphite ligands in the hydrocyanation of butadiene and t-3 pentenenitrile, and the isomerization of 2-methyl-3-butenenitrile
3PN hydrocyanation

| | BD hydrocyanation | Selectivity. . . |
|---------------------------------|--|------------------|
| IT 4635-87-4P, 3-Pentenenitrile | 16529-56-9P, 2-Methyl-3- butenenitrile | |
| | (polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles) | |

| | | |
|---|--|------------------|
| IT 74-90-8, Hydrogen cyanide, reactions | 10E-99-0, | |
| Butadiene, reactions | 592-51-8, 4-Pentenenitrile | 818-57-5, Methyl |
| 4-pentenoate | 818-58-6, Methyl 3-pentenoate | 818-59-7, Methyl |
| 2-pentenoate | | |
| | (polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles) | |

| | | |
|---------------|---|-----|
| PI US 6284865 | B1 20010904 | --> |
| AB | A polymeric composition, a process for producing the composition, and a process for using the composition in, for example, hydrocyanation or isomerization are disclosed. The composition comprises repeat units derived from (1) a carbonyl compound, a monomer, and phosphorochloridite; (2) phosphorus trichloride, a polyhydric alcohol, and an aromatic diol; or (3) combinations of (1) and (2) in which the monomer can be a polyhydric alcohol, an amine, combinations thereof. The composition can further comprise a Group VIII metal and optionally a Lewis acid. The composition can be produced by (1) contacting a carbonyl compound with the monomer to produce an intermediate and contacting the intermediate with phosphorochloridite; (2) contacting phosphorus trichloride with a second polyhydric alcohol under a condition sufficient to produce a phosphorus-containing polymer and contacting the phosphorus-containing polymer with an aromatic diol; or (3) contacting an N,N-dialkyl dichlorophosphoramidite with a second polyhydric alcohol to produce a polymer phosphoramidite, contacting the polymer phosphoramidite with an acid such as HCl to produce the phosphorus-containing polymer, which is then contacted with an aromatic diol. The composition can be used as catalyst, for example, for converting an unsaturated organic compound to a nitrile and isomerizing a nitrile. | |
| SUMM | This invention relates to a polymeric phosphite composition and polymeric phosphite catalyst composition that can be useful for a variety of catalytic processes, to a process for producing the composition, and to a process for using the composition in the hydrocyanation of unsaturated organic compounds and the isomerization of unsaturated nitriles. | |

SUMM Phosphorus-based ligands are ubiquitous in catalysis, finding use for

a number of commercially important chemical transformations. Phosphorus-based ligands commonly encountered in catalysis include phosphines and phosphites. Monophosphine and monophosphite ligands are compounds which contain a single phosphorus atom which serves as a donor to a transition metal. Bisphosphine, bisphosphite, and bisphosphorus ligands in general, contain two phosphorus donor atoms and typically form cyclic chelate structures with transition metals.

- SUMM Two industrially important catalytic reactions using phosphorus ligands of particular importance are olefin hydrocyanation and isomerization of branched nitrates to linear nitrates. Phosphine ligands are particularly good ligands for both reactions. The hydrocyanation of ethylenically unsaturated compounds using transition metal complexes with monodentate phosphite ligands is well documented in the prior art. See for example U.S. Pat. Nos. 3,496,215; 3,631,191; 3655,723; 3,766,237; and 5,543,536. Bidentate phosphite ligands have also been shown to be particularly useful ligands in the hydrocyanation of activated ethylenically unsaturated compounds. See for example, Baker, M. J., and Pringle, P. G., J. Chem. Soc., Chem. Commun., 1292, 1991; Baker et al., J. Chem. Soc., Chem. Commun., 803, 1991; WO 93,03839; U.S. Pat. Nos. 5,512,696; 5,723,641; 5,688,986.
- SUMM Recovery of the ligand and catalyst is important for a successful process. Typical separation procedures to remove the product(s) from the catalyst and ligand involve extraction with an immiscible solvent or distillation. It is usually difficult to recover the catalyst and ligand quantitatively. For instance, distillation of a volatile product from a non-volatile catalyst results in thermal degradation of the catalyst. Similarly, extraction results in some loss of catalyst into the product phase. For extraction, one would like to be able to tune the solubility of the ligand and catalyst to disfavor solubility in the product phase. These ligands and metals are often very expensive and thus it is important to keep such losses to a minimum for a commercially viable process.
- SUMM One method to solve the problem of catalyst and product separation is to attach the catalyst to an insoluble support. Examples of this approach have been previously described, and general references on this subject can be found in "Supported Metal Complexes", D. Reidel Publishing, 1985, Acta Polymer., 1996, 47,1; Comprehensive Organometallic Chemistry, Pergamon Press, 1982, Chapter 55; and Beller, M., Cornils, B., Frohning, C. D., Kohlpaintner, C. W., Journal of Molecular Catalysis A, 104, 1995, 17-85 and Macromol. Symp. 1994, 80, 241. Specifically, monophosphine and monophosphite ligands attached to solid supports are described in these references. Bisphosphine ligands have also been attached to solid supports and used for catalysis, as described in for example U.S. Pat. No. 5,432,289; J. Mol. Catal. A, 1996, 112,217; and J. Chem. Soc., Chem. Commun., 1996, 653. The solid support in these prior art examples can be organic, e.g., a polymer resin, or inorganic in nature.
- SUMM There is always a need to develop a composition that can be used as or in a catalyst with substantially reduced loss during a catalytic reaction or separation of product from the catalyst. An object of the present invention is, therefore, to provide such a composition and to provide processes for making and for using the composition.
- SUMM An advantage of the invention composition is that varying the molecular weight and degree of branching can control the solubility of the composition. Another advantage of the invention is that the catalyst

produced by the composition can be substantially recovered by filtration. Other objects and advantages of the present invention will become apparent as the invention is more fully disclosed below.

- SUMM According to a second embodiment of the invention, a composition that can be used as a catalyst is provided, which comprises (1) composition disclosed in the first embodiment, (2) a Group VIII metal selected from Ni, Co, Pd, and combinations of two or more thereof, and optionally (3) a Lewis acid.
- SUMM According to a sixth embodiment of the invention, a process is provided. The process comprises contacting, in the presence of a catalyst disclosed in the second embodiment of the invention, an unsaturated organic compound with a hydrogen cyanide-containing fluid under a condition sufficient to produce a nitrile.
- SUMM According to a seventh embodiment of the invention, a process is provided. The process comprises contacting a nitrile with the catalyst disclosed in the second embodiment of the invention to produce linear 3-alkenenitrile.
- SUMM These polyhydric alcohols can be produced by those skilled in the art. For example, the diacetal can be prepared by refluxing di(trimethylolpropane) with salicylaldehyde with oxalic acid as catalyst. For references for preparing acetal from acid catalyzed reaction of an aldehyde and an alcohol, see Tetrahedron, 1996, 14599; Tet. Lett., 1989, 1609; Tetrahedron, 1990, 3315. 1,3-bis(2-hydroxyphenoxy)propane was prepared by a literature procedure, J. Org. Chem., 48, 1983, 4867. 4,4'-ethylenebis(2,5-dimethylphenol); 4,4'-propylenebis(2,5-dimethylphenol); 4,4'-benzylidenebis(2,5-dimethylphenol); and 4,4'-ethylenebis(2-isopropyl-5-methylphenol) can be prepared according to Bull. Chem. Soc. Jpn., 62, 3603 (1989).
- SUMM The solubilities of these composition or polymeric phosphite ligands disclosed above generally depend on the molecular weight of the polymer and degree of branching. For soluble polymeric system, separation can therefore be done by extraction. With insoluble polymeric systems, the catalyst can be placed in fixed beds or separated by filtration from a reaction mixture. Alternatively, the solubility of the polymer can be adjusted to be soluble in the reactants and insoluble in the products. Thus, the reaction can be carried out homogeneously to obtain high conversion. The polymeric catalyst can then be separated by easy means such as decantation or filtration.
- SUMM According to the second embodiment of the invention, the compositions disclosed above can be combined with a Group VIII metal and, optionally, a Lewis acid to produce a catalyst composition. The term "Group VIII" refers to the ACS version of the Periodic Table of the Elements, 67.sup.th edition (1986-1987), CRC Handbook of Chemistry and Physics, Press, Boca Raton, Fla. The term "Group VIII metal" used in the invention can also refer to Group VIII metal compound or Group VIII metal complex.
- SUMM Generally, a Group VIII compound is combined with a polymer disclosed above to produce a desired catalyst. Among the Group VIII compounds, a nickel compound, a cobalt compound, or a palladium compound is preferred. A nickel compound is more preferred. A zero-valent nickel compound containing a ligand that can be displaced by the polymer is the most preferred source of Group VIII metal. Zero-valent nickel compounds can be prepared or generated according to means known in the art such as

disclosed in U.S. Pat. Nos. 3,496,217; 3,631,191; 3,846,461; 3,847,959 and 3,903,120. Two such preferred zero-valent nickel compounds are Ni(COD).sub.2 (COD is 1,5-cyclooctadiene) and Ni{P(0-o-C.sub.6 H.sub.4 CH.sub.3).sub.3 }.sub.2 (C.sub.2 H.sub.4), both of which are known in the art.

- SUMM Alternatively, divalent nickel compounds can be combined with a reducing agent, to serve as a source of zero-valent nickel in the reaction. Suitable divalent nickel compounds include compounds of the formula NiY.sub.2 where Y is halide, carboxylate, or acetylacetonate. Suitable reducing agents include metal borohydrides, metal aluminum hydrides, metal alkyls, Li, Na, K, or H.sub.2. Elemental nickel, preferably nickel powder, when combined with a halogenated catalyst, as described in U.S. Pat. No. 3,903,120, is also a suitable source of zero-valent nickel.
- SUMM The amount of transition metal can be any amount so long as favorable results can be obtained with respect to catalyst activity and process economy, when used as a catalyst. In general, the molar ratio of phosphorus ligand to transition metal generally can be from about 1:1 to about 100:1, preferably from about 1:1 to about 20:1 (moles phosphorus per mole metal).
- SUMM The composition of the second embodiment of the invention can further comprise one or more Lewis acid promoters that affect both the activity and the selectivity of the catalyst system. The promoter can be an inorganic or organometallic compound in which the promoter contains at least one element selected from scandium, titanium, vanadium, chromium, manganese, iron, cobalt, copper, zinc, boron, aluminum, yttrium, zirconium, niobium, molybdenum, cadmium, rhenium and tin. Examples include ZnBr.sub.2, ZnI.sub.2, ZnCl.sub.2, ZnSO.sub.4, CuCl.sub.2, CuCl, Cu(O.sub.3 SCF.sub.3).sub.2, CoCl.sub.2, CoI₂, FeI₂, FeCl₃, FeCl₂.sub.2, FeCl₂(THF).sub.2, TiCl₄.sub.2, TiCl₄.sub.4, TiCl₃.sub.3, ClTi(O*i*Pr).sub.3, MnCl₂.sub.2, ScCl₃.sub.3, AlCl₃.sub.3, (C₂H₅AlCl₂).sub.2, (C₂H₅AlCl₂).sub.2 AlCl, (C₂H₅AlCl₂).sub.2 AlCl, (iso-C₄H₉AlCl₂).sub.2 AlCl, PhAlCl₂, ReCl₅, ZrCl₄.sub.2, NbCl₅.sub.2, VCl₃.sub.3, CrCl₃.sub.2, MoCl₅.sub.2, YCl₃.sub.3, CdCl₂.sub.2, LaCl₃.sub.3, Er(O₃SCF₃).sub.3, Yb(O₃CCF₃).sub.3, SmCl₃.sub.3, B(C₂H₅AlCl₂).sub.2, TaCl₅.sub.5. Suitable promoters are further described in U.S. Pat. Nos. 3,496,217; 3,496,218 and 4,774,353. These include metal salts (such as ZnCl₂.sub.2, CoI₂.sub.2, and SnCl₂.sub.2), and organometallic compounds (such as RAlCl₂.sub.2, R₂Sn₃SnO₃.sub.3 SCF₃.sub.3, and R₂B₃ where R is an alkyl or aryl group). U.S. Pat. No. 4,874,884 describes how synergistic combinations of promoters can be chosen to increase the catalytic activity of the catalyst system. Preferred promoters include CdCl₂.sub.2, FeCl₂.sub.2, ZnCl₂.sub.2, B(C₂H₅AlCl₂).sub.2, and (C₂H₅AlCl₂).sub.2 SnX, where X.dbd.CF₃.sub.3 SO₃.sub.3, CH₂.sub.3 C₂H₅.sub.2 SO₃.sub.3, or (C₂H₅AlCl₂).sub.2 BCN. The mole ratio of promoter to Group VIII metal can be in the range of from about 1:1 to about 1000:1, preferably about 1:16 to about 50:1.

- SUMM According to the sixth embodiment of the invention, a process that can be used in organic compound conversions is provided. The process can comprise, consist essentially of, or consist of contacting, in the presence of a catalyst composition, an unsaturated organic compound with a hydrogen cyanide-containing fluid under a condition sufficient to produce a nitrile wherein the catalyst composition can be the same as that disclosed in the second embodiment of the invention. The term "fluid" can be gas, liquid, or both. Any fluid containing about 1 to

100% HCN can be used.

- SUMM The unsaturated organic compound can also be substituted with one or more functional groups containing a heteroatom, such as oxygen, sulfur, nitrogen or phosphorus. Examples of these heteroatom-substituted ethylenically unsaturated organic compounds include vinyl methyl ether, methyl oleate, oleyl alcohol, 3-pentenenitrile, 4-pentenenitrile, 3-pentenoic acid, 4-pentenoic acid, methyl 3-pentenoate, acrylonitrile, acrylic acid esters, methyl acrylate, methacrylic acid esters, methyl methacrylate, acrolein, allyl alcohol and combinations of two or more thereof.
- SUMM The hydrocyanation process can be carried out, for example, by charging a suitable vessel such as a reactor with an unsaturated compound, catalyst composition, and solvent, if any to form a reaction mixture. Hydrogen cyanide can be initially combined with other components to form the mixture. However, it is preferred that HCN is added slowly to the mixture after other components have been combined. Hydrogen cyanide can be delivered as a liquid or as a vapor to the reaction. As an alternative, a cyanohydrin can be used as the source of HCN. See, for example, U.S. Pat. No. 3,655,723.
- SUMM Another suitable technique is to charge the vessel with the catalyst and the solvent to be used, and feed both the unsaturated compound and the HCN slowly to the reaction mixture.
- SUMM The molar ratio of unsaturated compound to catalyst can be varied from about 10:1 to about 10000:1. The molar ratio of HCN to catalyst generally is varied from about 10:1 to 100,000:1, preferably 100:1 to 5,000:1, for a batch operation. In a continuous operation, such as when using a fixed bed catalyst type of operation, a higher proportion of catalyst can be used such as 5:1 to 100,000:1, preferably 100:1 to 5,000:1, HCN to catalyst.
- SUMM The hydrocyanation can be carried out with or without a solvent. The solvent, if used, can be liquid at the reaction temperature and pressure and inert towards the unsaturated compound and the catalyst. Suitable solvents include hydrocarbons such as benzene, xylene, or combinations thereof; ethers such as tetrahydrofuran (THF); nitrites such as acetonitrile, benzonitrile, adiponitrile, or combinations of two or more thereof. The unsaturated compound to be hydrocyanated can itself serve as the solvent. Hydrocyanation can also be carried out in gas phase.
- SUMM The exact temperature is dependent to a certain extent on the particular catalyst being used, the particular unsaturated compound being used and the desired rate. Normally, temperatures of from -25° C. to 200° C. can be used, the range of 0° C. to 150° C. being preferred.
- SUMM Examples of the unsaturated compounds include, but are not limited to, unsaturated organic compounds containing from 2 to approximately 30 carbon atoms. 3-Pentenenitrile and 4-pentenenitrile are especially preferred. When nonconjugated acyclic aliphatic monoethylenically unsaturated compounds are used, up to about 10% by weight of the monoethylenically unsaturated compound can be present in the form of a conjugated isomer, which itself may undergo hydrocyanation. For example, when 3-pentenenitrile is used, as much as 10% by weight thereof may be 2-pentenenitrile. (As used herein, the term "pentenenitrile" is intended to be identical with "cyanobutene"). Suitable unsaturated compounds include unsubstituted hydrocarbons as well as hydrocarbons substituted

with groups, which do not attack the catalyst, such as cyano. These unsaturated compounds include, but are not limited to, monoethylenically unsaturated compounds containing from 2 to 30 carbons such as ethylene, propylene, butene-1, pentene-2, hexene-2, and combinations of two or more thereof; nonconjugated diethylenically unsaturated compounds such as allene, substituted compounds such as 3-pentenenitrile, 4-pentenenitrile, methyl pent-3-enoate, and combinations of two or more thereof; and ethylenically unsaturated compounds having perfluoroalkyl substituents such as, for example, C_{sub.z}F_{sub.2z+1}, where z is an integer of up to 20. The monoethylenically unsaturated compounds can also be conjugated to an ester group such as methyl pent-2-enoate.

SUMM The process of the invention can be carried out in the presence of one or more Lewis acid promoters that affect both the activity and the selectivity of the catalyst system. The promoter is the same as that disclosed above.

SUMM For example, 2-alkyl-3-monoalkenenitrile used as the starting material in the isomerization of the invention can result from the hydrocyanation of a diolefin disclosed above or can come from any other available sources. The olefinic double bond in the 2-alkyl-3-monoalkenenitriles used as the starting materials in the isomerization of this invention cannot be conjugated to the triple bond of the cyano group. Suitable starting 2-alkyl-3-monoalkenenitriles can also carry groups that do not attack the catalyst, for example, another cyano group. Preferably, the starting 2-alkyl-3-monoalkenenitriles contain from 5 to 8 carbon atoms, excluding any additional substitution. 2-Methyl-3-butenenitrile is especially important in the production of adiponitrile. Other representative nitriles include 2-ethyl-3-butenenitrile and 2-propyl-3-butenenitrile.

SUMM The process can be carried out in the absence or in the presence of a solvent or diluent. Any solvent or diluent that is inert to or nondestructive of the catalyst can be used, however. Suitable solvents include, but are not limited to, aliphatic or aromatic hydrocarbons (hexane, cyclohexane, benzene), ethers (diethyl ether, tetrahydrofuran, dioxane, glycol dimethyl ether, anisole), esters (ethyl acetate, methyl benzoate, THF), nitriles (acetonitrile, benzonitrile), or combinations of two or more thereof.

SUMM A nonoxidizing environment is desirable in order to retard oxidative deactivation of the catalyst. Accordingly, an inert atmosphere, e.g., nitrogen, is preferably used, although air can be used if desired at the expense of loss of a proportion of the catalyst through oxidation.

SUMM The nickel complex is essentially nonvolatile, whereas the 2-methyl-3-butenenitrile reactant and the linear pentenenitrile products are relatively volatile. Accordingly, in a continuous flow procedure, the catalyst can be a component of the flowing system in a completely liquid-phase operation. It can also be in a mobile nonflowing liquid state in a semi-vapor phase operation, or it may be in a fixed-bed state in a conventional flowing vapor-phase operation.

SUMM The molar ratio of 2-alkyl-3-monoalkenenitrile to catalyst is generally greater than 1:1, usually in the range from about 5:1 to 20,000:1, preferably 100:1 to 5,000:1, for a batch or continuous operation.

DETD The following non-limiting, representative examples illustrate the process and catalyst compositions of this invention. All parts,

proportions, and percentages are by weight, unless otherwise indicated. In each example, the following procedure was used unless otherwise noted.

- DETD A catalyst solution was prepared by warming 0.1 g Fascat 4102 (butyltin tris(2-ethylhexanoate)) and 10 g of 1,6-hexanediol on the hot plate in a small vial with a small magnet. The solution was kept warm. A mixture containing 5 g of dimethyl 2,2'-dihydroxy-1,1'-binaphthalene-3,3'-dicarboxylate (0.0123 mmoles; reference for preparation; see J. Am. Chem. Soc., 1954, 76,296 and Tetrahedron Lett., 1990, 413), 2.6 g of 1,6-hexanediol and 1.75 g of warm catalyst solution was placed in a 25 ml microware 1-neck rb (round bottom) flask connected to a distillation head and receiver with a pre-calibrated heating mantle while stirring magnetically until methanol started to distill off (the temperature was about 180° C. at which temperature the dimethyl 2,2'-dihydroxy-1,1'-binaphthalene-3,3'-dicarboxylate had all dissolved). The temperature was then increased until the 1,6-hexanediol started to reflux in the top of the flask (220° C.). The mixture was allowed to reflux for about an hour and then house vacuum was gradually applied. Full pump vacuum was then applied to distill off the excess 1,6-hexanediol. The pressure was lowered very slowly to 4 mm Hg over the next two hours in order to avoid bumping. The reaction mixture was then polymerized at 270° C. for 2 hours while distilling off most of the 1,6-hexanediol. After cooling, the reaction mixture was refluxed with 25 ml of acetone for three hours and then cooled and filtered. NMR indicated degree of polymerization to be 6.
- DETD Preparation of catalyst: A catalyst solution was prepared by adding 0.039 g of Ni(COD)₂ (0.14 mmol) to 0.397 g of polyesterl (0.42 mmol of bidentate phosphite equivalents; the unit formula weight of the polymers were determined based on the expected formula) in 4.568 g toluene.
- DETD Hydrocyanation of butadiene: 74 µl of the above catalyst solution (0.0019 mmol Ni) were added to 2 reaction vials fitted with septum caps. The vials were cooled to -20° C. and 120 µl of a solution of HCN in valeronitrile (0.830 mmol HCN) and 280 µl of a solution of butadiene (BD) in toluene (0.925 mmol BD) were added to each vial. The vials were sealed and placed in a hot-block reactor set at 80° C. Samples were removed after 1.5 and 3 hours and quenched by cooling to -20° C. The reaction mixtures were then diluted in ethyl ether and the product distribution analyzed by GC against valeronitrile as an internal standard. Analysis showed that 67.5 and 68.7% of the starting HCN had been converted to useful pentenenitriles (the 3-pentenenitrile to 2-methyl-3-butenenitrile ratio was 1.1) after 1.5 and 3 hours respectively.
- DETD Isomerization of 2-methyl-3-butene nitrile (2M3BA): 82 µl of the above catalyst solution (0.0021 mmol Ni) were added to 2 reaction vials fitted with septum caps. 130 µl of a cold solution containing 2M3BN and valeronitrile (0.930 mmol 2M3BN) were added to each vial. The vials were sealed and placed in a hot block reactor set at 125° C. Samples were removed after 1.5 and 3.0 hrs, cooled and diluted in ethyl ether. The product distribution was analyzed by GC using valeronitrile as an internal standard. The 3PN/2M3BN ratio was 3.88 after 1.5 hrs and 5.50 after 3 hours.
- DETD Hydrocyanation of 3,4 Pentenenitrile (3,4 PN): 116 µl of the above catalyst solution (0.0030 mmol Ni), and 13 µl of a solution of ZnCl₂.sub.2 in 3PN (0.0067 mmol ZnCl₂.sub.2) were added to a vial fitted with a septum cap. The vial was cooled to -20° C. and 125 µl of a solution of HCN, t-3PN, and 2-ethoxyethyl ether (0.396 mmol HCN, 0.99 mmol t-3PN) was added. The vial was sealed and set aside for 24

- hours at room temperature. The reaction mixture was diluted with ethyl ether and the product distribution analyzed by GC using 2-ethoxyethyl ether as an internal standard. Analysis showed that 35.3% of the starting pentenenitriles had been converted to dinitrile product (88.1% yield based on HCN.) The selectivity to the linear ADN isomer was 92.7%.
- DETD 1. A 75-cc stainless steel autoclave equipped with a glass sleeve was charged with 3.05 g (21 mmol) N,N'-dimethyl-1,6-hexanediamine, 30 g deionized water, and 10.9 g (21 mmol) diphenyl 2,2'-dihydroxy-1,1'-binaphthalene-3,3'-dicarboxylate. The reactor contents were purged with nitrogen.
- DETD Preparation of catalyst. 0.059 g of branched polymer 1 was weighed into each of 3 reaction vials equipped with septum caps. 200 μ l of THF were added to each vial and the sample shaken. 320 μ l of a freshly made solution containing 0.015 mmol Ni(COD).sub.2 in toluene were added to each vial.
- DETD Hydrocyanation of butadiene: One of the catalyst samples prepared above was cooled to -20° C. and 280 μ l of a solution of butadiene in toluene (0.925 mmol BD) and 120 μ L of a solution of HCN in valeronitrile (0.830 mmol HCN) were added to the vial. The vial was sealed and heated at 80° C. for 3 hours. After a quench by cooling to -20° C., the reaction mixture was then diluted in ethylether and the product distribution analyzed by GC against valeronitrile as an internal standard. Analysis showed that 71.7% of the starting HCN had been converted to useful pentenenitriles (ratio of 3PN/2M3BN was 1.36) after 3 hours.
- DETD Isomerization of 2-methyl-3-butene nitrile (2M3BN): 130 μ l of a cold solution containing 2M3BN and valeronitrile (0.930 mmol 2M3BN) were added to one of the catalyst samples prepared above. The vial was sealed and heated at 125° C. for 3.0 hours. The reaction mixture was then cooled and diluted in ethyl ether. The product distribution was analyzed by GC using valeronitrile as an internal standard. The 3PN/2M3BN ratio was 0.47 after 3 hrs.
- DETD Hydrocyanation of 3,4 Pentenenitrile (3,4 PN): One of the catalyst samples prepared above was cooled to -20° C. and 125 μ l of a solution of HCN, t-3PN, and 2-ethoxyethyl ether (0.396 mmol HCN, 0.99 mmol t-3PN) was added. 13 μ l of a solution of ZnCl.sub.2 in 3PN (0.0067 mmol ZnCl.sub.2) were added to the vial. The vial was sealed and set aside for 24 hours at room temperature. The reaction mixture was diluted with ethyl ether and the product distribution analyzed by GC using 2-ethoxyethyl ether as an internal standard. Analysis showed that 23.4% of the starting pentenenitriles had been converted to dinitrile product (64.6% yield based on HCN.) The selectivity to the linear ADN isomer was 91.8%.
- DETD Preparation of catalyst: 0.056 g of branched polymer 2 was weighed into each of 3 reaction vials equipped with septum caps. 200 μ l of THF were added to each vial and the sample shaken. 320 μ l of a freshly made solution of 39 mg Ni(COD).sub.2 in 2.79 g toluene (0.015 mmol Ni) were added to each vial.
- DETD Hydrocyanation of butadiene: One of the catalyst samples prepared above was cooled to -20° C. and 280 μ l of a solution of butadiene in toluene (0.925 mmol BD) and 120 μ l of a solution of HCN in valeronitrile (0.830 mmol HCN) were added to the vial. The vial was sealed and placed in a hot-block reactor set at 80° C. The sample was removed after 3 hours and quenched by cooling to -20° C. The reaction mixture was then diluted in ethylether and the product distribution analyzed by GC against valeronitrile as an internal standard. Analysis showed that 84.8% of the starting HCN had been converted to useful pentenenitriles (ratio of 3PN/2M3BN was 0.51) after

3 hours.

- DETD Isomerization of 2-methyl-3-butene nitrile (2M3BN): 130 μ l of a cold solution containing 2M3BN and valeronitrile (0.930 mmol 2M3BN) were added to one of the catalyst samples prepared above. The vial was sealed and placed in a hot block reactor set at 125° C. The sample was removed after 3.0 hours, cooled and diluted in ethyl ether. The product distribution was analyzed by GC using valeronitrile as an internal standard. The 3PN/2M3BN ratio was 0.8 after 3 hrs.
- DETD Hydrocyanation of 3,4 Pentenenitrile (3,4 PN): One of that catalyst samples prepared above was cooled to -20° C. and 125 μ l of a solution of HCN, t-3PN, and 2-ethoxyethyl ether (0.396 mmol HCN, 0.99 mmol t-3PN) was added. 13 μ l of a solution of ZnCl₂.sub.2 in 3PN (0.0067 mmol ZnCl₂.sub.2) were added to the vial. The vial was sealed and set aside for 24 hours at room temperature. The reaction mixture was diluted with ethyl ether and the product distribution analyzed by GC using 2-ethoxyethyl ether as an internal standard. Analysis showed that 1.8% of the starting pentenenitriles had been converted to dinitrile product (5.0% yield based on HCN). The selectivity to the linear ADN isomer was 90.0%.
- DETD In the representative examples in Table 1 the polymeric phosphite was prepared from one of the polyhydeic alcohol 1-8 and one of aromatic diol A-E. Examples 7-9 and 13-14 illustrate the importance of control of polymer morphology on catalyst activity and selectivity.
- DETD TABLE 1
Selectivity and activity of several catalysts comprising polymeric phosphite ligands in the hydrocyanation of butadiene and t-3 pentenenitrile, and the isomerization of 2-methyl-3-butenenitrile

3PN hydrocyanation

| Example | diol | bridge | BD hydrocyanation | | Selectivity to Isomerization | |
|------------------|------|--------|-------------------|---------|------------------------------|------|
| | | | yield.sup.a) | 3PN/2M3 | yield.sup.a) | ADN |
| 3PN/2M3BN | | | | | | |
| 7.sup.b,d) | 1 | A | 29.5 | 0.9 | 66.5 | 88.8 |
| 8.sup.c,e) | 1 | A | 76.9 | 1.9 | 59.0 | 88.6 |
| 9.sup.c,f) | 1 | A | 77.1 | 8.2 | 63.0 | 89.7 |
| 10.sup.c) | 1 | B | 32.0 | 0.7 | 50.2 | 80.7 |
| 11.sup.c) | 1 | D | 68.2 | 1.5 | 50.8 | 87.1 |
| 12.sup.c,g) | 1 | E | 74.0 | 0.8 | 49.5 | 83.6 |
| 13.sup.c,h) | 1 | E | 70.1 | 1.0 | 67.0 | 88.4 |
| 14.sup.c) | 2 | C | 83.5 | 1.2 | 43.5 | 78.7 |
| 15.sup.c) | 3 | A | 69.9 | 31.5 | 59.5 | 92.8 |
| 16.sup.c) | 5 | C | 74.4 | 18.2 | 62.5 | 90.1 |
| 17.sup.c) | 4 | A | 73.8 | 2.5 | 38.5 | 94.4 |
| 18.sup.c) | 6 | A | 73.6 | 19.5 | 63.3 | 91.9 |
| 19.sup.c) | 7 | A | 86.0 | 2.7 | 50.8 | 95.5 |
| 20.sup.c) | 7 | C | 86.5 | 1.3 | 12.0 | 94.7 |
| 21.sup.c) | 8 | D | 84.5 | 2.5 | 31.25 | 89.9 |

.sup.a) Yield in % based on HCN.

.sup.b) Hydrocyanation and isomerization procedure analogous to that in Example 1A.

.sup.c) Hydrocyanation and isomerization procedure analogous to that in Example 4A.

.sup.d) 770 mg 1 were added to 412 mg PCl₂.sub.3 in a mixture of 30 ml toluene and 20 ml THF at -30° C. 800 mg NET₂.sub.3 in 20 ml toluene at -30° C. were added. Stirred 60 hrs. Added 363 mg A and 700 mg NET₂.sub.3 in 10 ml THF. Product was isolated by filtration..sup.e) 650 mg NET₂.sub.3 in 5 ml THF were added to 412 mg PCl₂.sub.3 and 769 mg 1 in 15 ml THF at -30° C. over a period of 10 minutes. 3 ml THF were added and the slurry cooled in a -30° C. freezer. 363 mg A and 650 mg NET₂.sub.3 were added, resulting in a gel. 15 ml THF were added and

the solution filtered. Solids were washed with hot H₂O, then with acetone, CH₂=CH-CN and THF.

.sup.f) 650 mg NEt₃ sub.3 in 15 ml THF were cooled to -30° C. and added to 412 mg PCl₃ and 769 mg l in 20 ml of THF at -30° C. The slurry was cooled after the addition. 363 mg A and 650 mg NEt₃ sub.3 were added. The solution was filtered and solids washed with THF. The polymer was THF soluble.

.sup.g) 412 mg PCl₃ and 769 mg l in 20 ml toluene and 20 ml THF were cooled to -30° C. in a freezer. 800 mg NEt₃ sub.3 in 20 ml toluene were added and the mixture cooled to -30° C. 790 mg E and 700 mg NEt₃ sub.3 were added. The mixture was filtered, washed with THF and the product recovered by removal of the solvent.

.sup.h) 1.679 g l was dissolved in 17 g toluene. 900 mg of PCl₃ were added. 5 g N(nBu)₃ in 8.7 g toluene were cooled to -30° C. and added to the mixture. 1.727 g E, 2.6 g N(nBu)₃, and 20 ml toluene were added and the mixture stirred. The product was isolated by addition of CH₂=CH-CN, filtration and washing with CH₂=CH-CN.

IT 4635-87-4P, 3-Pentenenitrile 16529-56-9P, 2-Methyl-3-butenenitrile
 (polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)

IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,
 Butadiene, reactions 592-51-8, 4-Pentenenitrile 818-57-5, Methyl 4-pentenoate 818-58-6, Methyl 3-pentenoate 818-59-7, Methyl 2-pentenoate
 (polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)

IT 4635-87-4P, 3-Pentenenitrile
 (polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)

RN 4635-87-4 USPATFULL
 CN 3-Pentenenitrile (CA INDEX NAME)



IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,
 Butadiene, reactions
 (polymeric phosphite catalysts for hydrocyanation of unsatd. organic compds. and isomerization of unsatd. nitriles)

RN 74-90-8 USPATFULL
 CN Hydrocyanic acid (CA INDEX NAME)



RN 106-99-0 USPATFULL
 CN 1,3-Butadiene (CA INDEX NAME)



L88 ANSWER 57 OF 60 USPATFULL on STN
ACCESSION . . .

AB The disclosure is a process for preparing mixtures of monoolefinic C.sub.5 mononitriles having nonconjugated C.dbd.C-- and C.tbd.N bonding by catalytic hydrocyanation of a hydrocarbon mixture containing 1,3-butadiene, by first diminishing the proportion of those components in the hydrocarbon mixture which impair the catalytic hydrocyanation and then subjecting the resulting mixture to catalytic hydrocyanation. CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB The disclosure is a process for preparing mixtures of monoolefinic C.sub.5 mononitriles having nonconjugated C.dbd.C-- and C.tbd.N bonding by catalytic hydrocyanation of a hydrocarbon mixture containing 1,3-butadiene, by first diminishing the proportion of those components in the hydrocarbon mixture which impair the catalytic hydrocyanation and then subjecting the resulting mixture to catalytic hydrocyanation.

SUMM . . . mononitriles in which the C.dbd.C bond and the C.tbd.N bond are not conjugated, to a process for their preparation by catalytic hydrocyanation of a 1,3-butadiene-containing hydrocarbon mixture, and to their use as intermediates for further processing to adiponitrile.

SUMM . . . way of removing acetylenes and allenes from diolefin-containing hydrocarbon mixtures consists in partly hydrogenating these mixtures in the presence of catalysts capable of differentiating between these classes of substances. For instance, U.S. Pat. No. 4,587,369 describes selective hydrogenation catalysts based on Pd on an alumina support.

SUMM U.S. Pat. No. 4,704,492 describes Cu/Pd catalysts useful as selective hydrogenation catalysts.

SUMM . . . for example 1,3-butadiene, while at the same time maximizing the removal of the acetylenes. U.S. Pat. No. 4,493,906 describes a catalyst based on finely divided copper on a γ -Al₂O₃ support with which acetylene is removed virtually completely from a butadiene-containing. . .

SUMM . . . 150° C. and at atmospheric pressure. Nickel complexes with phosphine or phosphite ligands and metal salt promoters are used as catalysts. The abovementioned review contains no mention of a possible utility of an industrial C.sub.4 cut instead of pure 1,3-butadiene as. . .

SUMM Applied Homogeneous Catalysis with Organometallic Compounds, Vol. 1, VCH Weinheim, pages 465 et seq., describes the heterogeneously and homogeneously catalyzed addition of hydrogen cyanide to olefins in general terms. Catalysts used are especially catalysts based on phosphine and phosphite complexes of nickel and palladium which permit a high product selectivity, improved conversions and shortened reaction times. Adiponitrile is prepared by hydrocyanation of butadiene using in the main nickel(0) phosphite catalysts, optionally in the presence of a Lewis acid as promoter. In general, the reaction can be divided into three steps: . . . the selectivity in respect of the linear 3-pentenenitrile is within the range from about 70 to 90%, depending on the catalyst used. If this first reaction step is carried out in the absence of Lewis acids, generally no second addition of hydrogen cyanide takes place and the resulting product mixture can be subjected to an isomerization using the same catalyst systems as in the first reaction step, this time in the presence of a Lewis acid, for example ZnCl₂, as. . . which the C,N triple bond is conjugated with the C,C double bond, inhibits the reaction, since it acts as a catalyst poison. The desired isomerization to 4-pentenenitrile is only possible as a result

SUMM of the fact that 3-pentenenitrile is isomerized significantly. . . EP-A-0 274 401 describes a process for hydrocyanating pure butadiene using a nickel catalyst containing a mixture of phenyl and m,p-tolyl phosphite ligands.

SUMM EP-A-315 551 describes a process for hydrocyanating pure dienes, for example 1,3-butadiene, 1,3-hexadiene, etc., by catalysis with a nickel(0) catalyst which contains an acid as promoter.

SUMM . . . mixture of alkenes and alkadienes by reacting the mixture with hydrogen cyanide in the presence of a nickel(0) complex as catalyst. The alkadienes react preferentially to form the corresponding nitriles and can be separated from the unconverted alkenes. Such an alkene-alkadiene. . .

SUMM . . . completely from the nonconjugated products of value, 3-pentenenitrile and 2-methyl-3-butenenitrile, are not further hydrocyanable to adiponitrile and are also pronounced catalyst poisons.

SUMM . . . in a first aspect a process for preparing mixtures of monoolefinic C._{sub}.5 mononitriles having nonconjugated C.dbd.C-- and C.tbd.N bonding by catalytic hydrocyanation of a hydrocarbon mixture containing 1,3-butadiene, by first diminishing the proportion of those components in the hydrocarbon mixture which impair the catalytic hydrocyanation and then subjecting the resulting mixture to catalytic hydrocyanation.

SUMM Components which give rise to catalyst poisons under catalytic hydrocyanation, especially alkynes, 1,2-dienes and mixtures thereof, are partially or completely removed from the hydrocarbon mixture.

SUMM . . . which a C.dbd.C double bond is conjugated with the C.tbd.N bond. As mentioned above, it is known from Applied Homogeneous Catalysis with organometallic Compounds, Vol. 1, VCH Weinheim, page 479, that the conjugated 2-pentenenitrile formed in the isomerization of 2-methyl-3-butenenitrile and. . . form adiponitrile. It was found that the abovementioned conjugated nitriles obtained on hydrocyanating an unpretreated C._{sub}.4 cut also act as catalyst poisons for the first reaction step of adiponitrile production, the monoaddition of hydrogen cyanide. Direct consequences are a distinctly diminished catalytic activity of the homogeneous nickel catalyst, lower conversions and lower nickel retrieval rates in catalyst recovery. The disadvantages can be avoided, as is shown in the experimental part.

SUMM . . . as well. These components are removed by subjecting the C._{sub}.4 cut prior to the addition of hydrogen cyanide to a catalytic partial hydrogenation. This partial hydrogenation takes place in the presence of a hydrogenation catalyst capable of selectively hydrogenating alkynes and 1,2-dienes in the presence of other dienes and monoolefins.

SUMM Suitable catalysts for the selective hydrogenation are known from the prior art and include customary homogeneous and heterogeneous hydrogenation catalyst systems. The catalysts suitable for the process of the invention are preferably based on a transition metal of the 8th or 1st subgroup, preference being given to using catalysts based on Ni, Pd, Pt, Ru or Cu. Particular preference is given to using catalysts based on Cu or Pd.

SUMM Suitable heterogeneous catalyst systems generally comprise one of the aforementioned transition metal compounds on an inert support. Suitable inorganic supports are the customary oxides, especially silicas and aluminas, aluminosilicates, zeolites, carbides, nitrides, etc. and mixtures thereof. Preferred supports are Al._{sub}.2 O._{sub}.3, SiO._{sub}.2 and mixtures thereof. The heterogeneous catalysts used in the process of the invention are in particular those described in U.S. Pat. No. 4,587,369; U.S. Pat. No. 4,704,492 and U.S. Pat. No. 4,493,906, which are all fully incorporated herein by reference. Further suitable Cu-based catalyst systems are marketed by Dow Chemical as KLP catalyst.

SUMM a) feeding the partly hydrogenated C._{sub}.4 cut, hydrogen cyanide and

hydrocyanation catalyst into a reactor,

SUMM e) working up the liquid and solid reactor effluent by distillation and recycling the recovered catalyst into the reactor.

SUMM The three components of the reaction mixture, hydrogen cyanide, partly hydrogenated C_{sub.4} cut and catalyst, are generally fed in separate feeds at the rate of their respective consumption. If instead of a homogeneous catalyst, which can be introduced into the reactor for example separately as a solution in a suitable solvent or together with one of the other feeds, a heterogeneous catalyst is used, the latter can also be preinstalled in the reactor in a suitable form.

SUMM . . . effluent is subjected to a distillative workup to isolate the desired products 3-pentenenitrile and 2-methyl-3-butenenitrile and also to recover the catalyst present. The recovered active catalyst is recycled into the reactor.

SUMM a) filling a pressure-resistant reactor with the partly hydrogenated C_{sub.4} cut, hydrogen cyanide and a hydrocyanation catalyst and optionally a solvent,

SUMM The pressure-resistant reactor is charged with the partly hydrogenated C_{sub.4} cut, hydrogen cyanide, a hydrocyanation catalyst and optionally a solvent before commencement of the reaction. Examples of suitable solvents are aromatic hydrocarbons, such as toluene and. . .

SUMM . . . extraction and the distillative workup of the remaining reaction mixture to remove the products of value and recover still active catalyst.

SUMM Suitable catalysts for the hydrocyanation are known from the prior art and include heterogeneous and preferably homogeneous catalyst systems. In general, catalysts suitable for the process of the invention are based on a transition metal of the 8th subgroup and optionally comprise a metal salt as promoter. The catalyst system used for the monoaddition of hydrogen cyanide preferably contains no addition of promoter.

SUMM The process of the invention is preferably carried out using at least one homogeneous catalyst selected from salts or complexes of nickel. Of particular suitability are Ni(0) complexes with phosphine, phosphinite, phosphonite or preferably phosphite. . .

SUMM The aforementioned catalysts can be used combined with a promoter, if desired. The promoter used is preferably a Lewis acid, for example AlCl_{sub.3} or ZnCl_{sub.2}. The catalysts used for the monoaddition of hydrogen cyanide preferably contain no addition of a promoter.

SUMM . . . to form various n-pentenenitriles. The proportion of 3-pentenenitrile formed should be as high as possible and the proportion of conjugated, catalyst-poisoning 2-pentenenitrile and 2-methyl-2-butenenitrile should be as low as possible.

SUMM The nickel phosphite catalysts preferred for the novel preparation of monoolefinic nitriles in step 1 are advantageously also suitable for the position and double. . .

SUMM . . . C_{sub.4} cut pretreated according to the invention. Since the continuous process is carried out with recycling of the active nickel catalyst, and the catalyst is added to the reaction mixture only in small amounts, even a slight hydrogen cyanide excess due to incomplete conversion. . . adverse effect on the nickel balance of the reaction. Thus, the continuous process of the invention surprisingly has a higher catalyst recycling rate and so longer catalyst on-stream times than known processes. This is also relevant from ecological aspects, since the nickel cyanide formed from the active catalyst and hydrogen cyanide is highly toxic and has to be expensively worked up or disposed of.

SUMM . . . which are isomerizable to 4-pentenenitrile, such as 3-pentenenitrile and 2-methyl-3-butenenitrile. Furthermore, the proportion of conjugated 2-pentenenitrile, which acts as a catalyst

- poison, is low and is preferably below 1% by weight, especially within the range from about 0.1 to 0.2% by. . .
- SUMM . . . form products having a C,C double bond conjugated with the nitrile function. Owing to the effect of these compounds as catalyst poisons, the nickel retrieval rates and the catalyst on-stream times are lower than in the process of the invention. Lower catalyst activities lead to lower conversions.
- SUMM . . . 1,3-butadiene-containing hydrocarbon mixture which additionally includes at least one alkyne and/or 1,2-diene with hydrogen in the presence of a hydrogenation catalyst.
- SUMM The present invention further provides a process for preparing adiponitrile, which comprises catalytically hydrocyanating a C.sub.5 mononitrile mixture prepared as described above, optionally after further workup or isomerization.
- DETD Catalyst Composition
- DETD Partly hydrogenated C.sub.4 cut, catalyst solution and hydrogen cyanide are introduced into a two stage stirred tank battery (pressure: 15 bar, temperature of reactor 1: . . . scrubbing tower. Liquid/solid effluents are analyzed, worked up by distillation to remove the products of value and recover still active catalyst, and the products thus obtained are again analyzed. The HCN conversions are determined by volumetric analysis of the reactor solutions from the two reactors. The nickel retrieval rate (recovery of active catalyst) is determined by means of elemental analysis.
- DETD An unhydrogenated hydrocarbon mixture of the above-specified composition is reacted similarly to Example 1, except that the catalyst feed is raised from 2.72 mmol/h to 4.85 mmol/h. The results are likewise reproduced in Table 1.
- DETD . . . the deficient component should have increased with increasing amount of excess component. Comparative Example 2, which utilizes a distinctly higher catalyst content, still does not match the results of Example 1.
- DETD 4.7 g of catalyst composition containing:
- DETD . . . 20.3 g of partially hydrogenated C.sub.4 cut (corresponding to 7.9 g (0.14 mol) of 1,3-butadiene), 2.75 g of a mixed catalyst (composition: 0.69 g (0.468 mmol) of tetrakis(tri-m/p-tolylphosphite)nickel(0), 1.65 g (4.68 mmol) of tri-m/p-tolylphosphite and 0.41 g 3-pentene nitrile) and 40. . .
- CLM What is claimed is:
1. A process for preparing mixtures of monoolefinic C.sub.5 mononitriles having nonconjugated C.dbd.C and C.tbd.N bonding by catalytic hydrocyanation of a hydrocarbon mixture containing 1,3-butadiene, wherein the hydrocarbon mixture is reacted with hydrogen in the presence of a hydrogenation catalyst capable of hydrogenating alkynes and 1,2-dienes with high selectivity without significantly diminishing the 1,3-butadiene content in order to remove alkynes, . . . and mixtures thereof partially or completely so that the proportion of those components in the hydrocarbon mixture which impair the catalytic hydrocyanation is diminished and then subjecting the resulting mixture to catalytic hydrocyanation.
 5. The process of claim 1, wherein the hydrocyanation catalyst catalyzes the position isomerization and double bond isomerization of the hydrocarbon mixture and/or of the nitriles as well as the hydrogen.
 7. A process for preparing adiponitrile, which comprises catalytically hydrocyanating a C.sub.5 mononitrile mixture prepared as claimed in any of claims 1 to 6, optionally after further workup or. . .
- IT 106-99-0, Butadiene, reactions
(hydrocyanation in purified C4 fractions)

IT 4635-87-4P, 3-Pentenenitrile 16529-56-9P, 2-Methyl-3-butenenitrile
 (monoolefinic C5 mononitrile production and use)

IT 74-90-8, Hydrocyanic acid, reactions
 (reaction with butadiene)

PI US 6197992 Bl 20010306
 WO 9827054 19980625

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AB The disclosure is a process for preparing mixtures of monoolefinic C.sub.5 mononitriles having nonconjugated C.dbd.C-- and C.tbd.N bonding by catalytic hydrocyanation of a hydrocarbon mixture containing 1,3-butadiene, by first diminishing the proportion of those components in the hydrocarbon mixture which impair the catalytic hydrocyanation and then subjecting the resulting mixture to catalytic hydrocyanation. |

SUMM The present invention relates to monoolefinic C.sub.5 mononitriles in which the C.dbd.C bond and the C.tbd.N bond are not conjugated, to a process for their preparation by catalytic hydrocyanation of a 1,3-butadiene-containing hydrocarbon mixture, and to their use as intermediates for further processing to adiponitrile.

SUMM One way of removing acetylenes and allenes from diolefin-containing hydrocarbon mixtures consists in partly hydrogenating these mixtures in the presence of catalysts capable of differentiating between these classes of substances. For instance, U.S. Pat. No. 4,587,369 describes selective hydrogenation catalysts based on Pd on an alumina support.

SUMM U.S. Pat. No. 4,704,492 describes Cu/Pd catalysts useful as selective hydrogenation catalysts.

SUMM For certain uses of the hydrocarbon mixture, it is desirable to minimize the loss of diolefin, for example 1,3-butadiene, while at the same time maximizing the removal of the acetylenes. U.S. Pat. No. 4,493,906 describes a catalyst based on finely divided copper on a γ-Al₂O₃ support with which acetylene is removed virtually completely from a butadiene-containing mixture and the butadiene loss is in the region of not more than 1%.

SUMM The last process produces in a first stage, by monoaddition, a mixture of isomeric pentenenitriles and methylbutenenitriles, which, in a second stage, is isomerized to predominantly 3- and 4-pentenenitrile. Subsequently, in a third stage, the adiponitrile is formed by anti-Markovnikov hydrogen cyanide addition to 4-pentenenitrile. The reaction takes place in the liquid phase in a solvent, for example tetrahydrofuran, at a temperature within the range from 30 to 150° C. and at atmospheric pressure. Nickel complexes with phosphine or phosphite ligands and metal salt promoters are used as catalysts. The abovementioned review contains no mention of a possible utility of an industrial C.sub.4 cut instead of pure 1,3-butadiene as reactant.

SUMM Applied Homogeneous Catalysis with Organometallic Compounds, Vol. 1, VCH Weinheim, pages 465 et seq., describes the heterogeneously and homogeneously catalyzed addition of hydrogen cyanide to olefins in general terms. Catalysts used are especially catalysts based on phosphine and phosphite complexes of nickel and palladium which permit a high product selectivity, improved conversions and shortened reaction times. Adiponitrile is prepared by hydrocyanation of butadiene using in the main nickel(0) phosphite catalysts, optionally in the presence of a Lewis acid as promoter. In general, the reaction can be divided into three steps: 1. synthesis of mononitriles by hydrocyanation of 1,3-butadiene; 2. isomerization; 3. synthesis of dinitriles. The

monoaddition product is an isomeric mixture of 3-pentenenitrile and 2-methyl-3-butenenitrile, and the selectivity in respect of the linear 3-pentenenitrile is within the range from about 70 to 90%, depending on the catalyst used. If this first reaction step is carried out in the absence of Lewis acids, generally no second addition of hydrogen cyanide takes place and the resulting product mixture can be subjected to an isomerization using the same catalyst systems as in the first reaction step, this time in the presence of a Lewis acid, for example ZnCl₂.sub.2, as promoter. The 2-methyl-3-butenenitrile isomerizes to 3-pentenenitrile on the one hand, and 3-pentenenitrile isomerizes to the various n-cyanonitriles on the other. The cited publication mentions that the thermodynamically most stable isomer, 2-pentenenitrile, in which the C,N triple bond is conjugated with the C,C double bond, inhibits the reaction, since it acts as a catalyst poison. The desired isomerization to 4-pentenenitrile is only possible as a result of the fact that 3-pentenenitrile is isomerized significantly more rapidly to 4-pentenenitrile than to 2-pentenenitrile.

- SUMM EP-A-0 274 401 describes a process for hydrocyanating pure butadiene using a nickel catalyst containing a mixture of phenyl and m,p-tolyl phosphite ligands.
- SUMM EP-A-315 551 describes a process for hydrocyanating pure dienes, for example 1,3-butadiene, 1,3-hexadiene, etc., by catalysis with a nickel(0) catalyst which contains an acid as promoter.
- SUMM U.S. Pat. No. 4,434,316 describes a process for removing the alkenes from a mixture of alkenes and alkadienes by reacting the mixture with hydrogen cyanide in the presence of a nickel(0) complex as catalyst. The alkadienes react preferentially to form the corresponding nitriles and can be separated from the unconverted alkenes. Such an alkene-alkadiene separation is necessary for example in industrial processes for the production of dinitriles in order that the alkenes, which cannot form dinitriles, can be separated from the alkadienes. The process described is suitable for separating alkenes having 2 to 5 carbon atoms, for example ethylene, propylene, butenes and propenes from alkadienes having 3 to 8 carbon atoms, for example propadiene, butadiene, pentadiene, hexadiene and octadiene. The presence of acetylenically and ethylenically unsaturated hydrocarbons is not considered disadvantageous for the separation process described. The reference does not mention the possibility of hydrocyanating a 1,3-butadiene-containing hydrocarbon mixture and especially a C.sub.4 cut from petroleum refineries to produce C.sub.5 monoolefin mixtures having a nitrile function.
- SUMM However, the prior art processes for hydrocyanating 1,3-butadiene-containing hydrocarbon mixtures have the disadvantage that conjugated butenenitriles and/or pentenenitriles are obtained as unwanted by-products. These conjugated butenenitriles and/or pentenenitriles are impossible to separate completely from the nonconjugated products of value, 3-pentenenitrile and 2-methyl-3-butenenitrile, are not further hydrocyanable to adiponitrile and are also pronounced catalyst poisons.
- SUMM The present invention accordingly provides in a first aspect a process for preparing mixtures of monoolefinic C.sub.5 mononitriles having nonconjugated C.dbd.C-- and C.tbd.N bonding by catalytic hydrocyanation of a hydrocarbon mixture containing 1,3-butadiene, by first diminishing the proportion of those components in the hydrocarbon mixture which impair the catalytic hydrocyanation and then subjecting the resulting mixture to catalytic hydrocyanation.

- SUMM Components which give rise to catalyst poisons under catalytic hydrocyanation, especially alkynes, 1,2-dienes and mixtures thereof, are partially or completely removed from the hydrocarbon mixture.
- SUMM Especially the hydrocyanation of a C.sub.4 cut which is not completely free from alkynes, for example propyne or butyne, from 1,2-dienes, for example propadiene, and from alkenes, for example vinylacetylene, affords products in which a C.dbd.C double bond is conjugated with the C.tbd.N bond. As mentioned above, it is known from Applied Homogeneous Catalysis with Organometallic Compounds, Vol. 1, VCH Weinheim, page 479, that the conjugated 2-pentenenitrile formed in the isomerization of 2-methyl-3-butenenitrile and 3-pentenenitrile acts as a reaction inhibitor for the second addition of hydrogen cyanide to form adiponitrile. It was found that the abovementioned conjugated nitriles obtained on hydrocyanating an unpretreated C.sub.4 cut also act as catalyst poisons for the first reaction step of adiponitrile production, the monoaddition of hydrogen cyanide. Direct consequences are a distinctly diminished catalytic activity of the homogeneous nickel catalyst, lower conversions and lower nickel retrieval rates in catalyst recovery. The disadvantages can be avoided, as is shown in the experimental part.
- SUMM The production of monoolefinic C.sub.5 mononitriles according to the process of the invention is preferably carried out using an industrially produced hydrocarbon mixture having a high proportion of 1,3-butadiene. An example of an industrially produced hydrocarbon mixture having a high proportion of 1,3-butadiene is the C.sub.4 cut which is obtained in petroleum processing by steam cracking of naphtha and which as a consequence of its method of production always contains alkynes and 1,2-dienes as well. These components are removed by subjecting the C.sub.4 cut prior to the addition of hydrogen cyanide to a catalytic partial hydrogenation. This partial hydrogenation takes place in the presence of a hydrogenation catalyst capable of selectively hydrogenating alkynes and 1,2-dienes in the presence of other dienes and monoolefins.
- SUMM Suitable catalysts for the selective hydrogenation are known from the prior art and include customary homogeneous and heterogeneous hydrogenation catalyst systems. The catalysts suitable for the process of the invention are preferably based on a transition metal of the 8th or 1st subgroup, preference being given to using catalysts based on Ni, Pd, Pt, Ru or Cu. Particular preference is given to using catalysts based on Cu or Pd.
- SUMM Suitable heterogeneous catalyst systems generally comprise one of the aforementioned transition metal compounds on an inert support. Suitable inorganic supports are the customary oxides, especially silicas and aluminas, aluminosilicates, zeolites, carbides, nitrides, etc. and mixtures thereof. Preferred supports are Al₂O₃, SiO₂ and mixtures thereof. The heterogeneous catalysts used in the process of the invention are in particular those described in U.S. Pat. No. 4,587,369; U.S. Pat. No. 4,704,492 and U.S. Pat. No. 4,493,906, which are all fully incorporated herein by reference. Further suitable Cu-based catalyst systems are marketed by Dow Chemical as KLP catalyst.
- SUMM a) feeding the partly hydrogenated C.sub.4 cut, hydrogen cyanide and hydrocyanation catalyst into a reactor,
- SUMM e) working up the liquid and solid reactor effluent by distillation and

recycling the recovered catalyst into the reactor.

- SUMM The three components of the reaction mixture, hydrogen cyanide, partly hydrogenated C_{sub.4} cut and catalyst, are generally fed in separate feeds at the rate of their respective consumption. If instead of a homogeneous catalyst, which can be introduced into the reactor for example separately as a solution in a suitable solvent or together with one of the other feeds, a heterogeneous catalyst is used, the latter can also be preinstalled in the reactor in a suitable form.
- SUMM The liquid and/or solid reactor effluent is subjected to a distillative workup to isolate the desired products 3-pentenenitrile and 2-methyl-3-butenenitrile and also to recover the catalyst present. The recovered active catalyst is recycled into the reactor.
- SUMM a) filling a pressure-resistant reactor with the partly hydrogenated C_{sub.4} cut, hydrogen cyanide and a hydrocyanation catalyst and optionally a solvent,
- SUMM The pressure-resistant reactor is charged with the partly hydrogenated C_{sub.4} cut, hydrogen cyanide, a hydrocyanation catalyst and optionally a solvent before commencement of the reaction. Examples of suitable solvents are aromatic hydrocarbons, such as toluene and xylene, or tetrahydrofuran.
- SUMM To complete the reaction, the reaction time can be followed by a postreaction time of from 0 minutes to about 5 hours, preferably from about 1 hour to 3 hours, during which no further hydrogen cyanide is introduced into the autoclave. The temperature during this period is left essentially constant at the previously set reaction temperature. The workup is carried out according to commonly used processes and comprises removing the unconverted 1,3-butadiene and the unconverted hydrogen cyanide, for example by washing or extraction and the distillative workup of the remaining reaction mixture to remove the products of value and recover still active catalyst.
- SUMM Suitable catalysts for the hydrocyanation are known from the prior art and include heterogeneous and preferably homogeneous catalyst systems. In general, catalysts suitable for the process of the invention are based on a transition metal of the 8th subgroup and optionally comprise a metal salt as promoter. The catalyst system used for the monoaaddition of hydrogen cyanide preferably contains no addition of promoter.
- SUMM The process of the invention is preferably carried out using at least one homogeneous catalyst selected from salts or complexes of nickel. Of particular suitability are Ni(0) complexes with phosphine, phosphinite, phosphonite or preferably phosphite ligands. Suitable nickel phosphine, phosphinite, phosphonite or phosphite complexes have the general formula NiL_{sub.4}, where L is PR_{sub.3}, P(OR)R_{sub.2}, P(OR)_{sub.2}R or P(OR)_{sub.3} and R is alkyl, cycloalkyl or aryl, preferably phenyl or m,p-tolyl. It is also possible to use mixtures of different radicals R. In a preferred embodiment, the reaction takes place in the presence of an Ni(0) complex which comprises at least one multidentate phosphine, phosphinite, phosphonite or phosphite ligand. Suitable phosphite chelators are described in WO 96/22968, U.S. Pat. No. 5,484,902, WO 96/11182, U.S. Pat. No. 5,523,453, WO 95/30680, WO 95/28228 and WO 95/14659, which are all fully incorporated herein by reference.

- SUMM The aforementioned catalysts can be used combined with a promoter, if desired. The promoter used is preferably a Lewis acid, for example AlCl₃.sub.3 or ZnCl₂.sub.2. The catalysts used for the monoaddition of hydrogen cyanide preferably contain no addition of a promoter.
- SUMM 2. Isomerization of the 2-methyl-3-butenenitrile in these mixtures to 3-pentenenitrile and isomerization of the resulting 3-pentenenitrile and of the 3-pentenenitrile already present in the mixtures from step 1 to form various n-pentenenitriles. The proportion of 3-pentenenitrile formed should be as high as possible and the proportion of conjugated, catalyst-poisoning 2-pentenenitrile and 2-methyl-2-butenenitrile should be as low as possible.
- SUMM The nickel phosphite catalysts preferred for the novel preparation of monoolefinic nitriles in step 1 are advantageously also suitable for the position and double bond isomerization in step 2 and the second addition of hydrogen cyanide in step 3. A suitable procedure involves for example the monoaddition of step 1 being carried out in the absence of promoters, for example Lewis acids such as ZnCl₂.sub.2, the isomerization of step 2 being carried out in the presence of Lewis acids, to optimize the yield of 3-pentenenitrile, and the second addition in step 3 being optionally carried out with the ZnCl₂.sub.2 having been replaced by triphenylboron to optimize the adiponitrile selectivity of the reaction.
- SUMM The industrially preferred continuous form of the process of the invention affords hydrogen cyanide conversions in the region of about 98% for unpretreated C.sub.4 cut under reaction conditions which are otherwise identical to those of the process of this invention compared with essentially complete conversions in the region of, for example, 99.8% on use of C.sub.4 cut pretreated according to the invention. Since the continuous process is carried out with recycling of the active nickel catalyst, and the catalyst is added to the reaction mixture only in small amounts, even a slight hydrogen cyanide excess due to incomplete conversion has a strongly adverse effect on the nickel balance of the reaction. Thus, the continuous process of the invention surprisingly has a higher catalyst recycling rate and so longer catalyst on-stream times than known processes. This is also relevant from ecological aspects, since the nickel cyanide formed from the active catalyst and hydrogen cyanide is highly toxic and has to be expensively worked up or disposed of.
- SUMM It is preferable to obtain a high proportion of 4-pentenenitrile and also of products which are isomerizable to 4-pentenenitrile, such as 3-pentenenitrile and 2-methyl-3-butenenitrile. Furthermore, the proportion of conjugated 2-pentenenitrile, which acts as a catalyst poison, is low and is preferably below 1% by weight, especially within the range from about 0.1 to 0.2% by weight, based on C.sub.4 cut used.
- SUMM As gas space analyses show, if C.sub.4 cut is used for the hydrocyanation which has not been partly hydrogenated, it is not only 1,3-butadiene which is hydrocyanated, but also the alkynes and 1,2-dienes present, to form products having a C,C double bond conjugated with the nitrile function. Owing to the effect of these compounds as catalyst poisons, the nickel retrieval rates and the catalyst on-stream times are lower than in the process of the invention. Lower catalyst activities lead to lower conversions.
- SUMM The invention further provides a process for selective hydrogenation of C.sub.4 cuts, which comprises reacting a 1,3-butadiene-containing hydrocarbon mixture which additionally includes at least one alkyne

and/or 1,2-diene with hydrogen in the presence of a hydrogenation catalyst.

- SUMM The present invention further provides a process for preparing adiponitrile, which comprises catalytically hydrocyanating a C._{sub.5} mononitrile mixture prepared as described above, optionally after further workup or isomerization.
- DETD Catalyst Composition
- DETD Partly hydrogenated C._{sub.4} cut, catalyst solution and hydrogen cyanide are introduced into a two stage stirred tank battery (pressure: 15 bar, temperature of reactor 1: 102° C., temperature of reactor 2: 95° C., residence time: 40 min/reactor). The effluent is stripped free from hydrocyanic acid and butadiene, the gas space is analyzed, and the gaseous effluent is passed through an NaOH scrubbing tower. Liquid/solid effluents are analyzed, worked up by distillation to remove the products of value and recover still active catalyst, and the products thus obtained are again analyzed. The HCN conversions are determined by volumetric analysis of the reactor solutions from the two reactors. The nickel retrieval rate (recovery of active catalyst) is determined by means of elemental analysis.
- DETD An unhydrogenated hydrocarbon mixture of the above-specified composition is reacted similarly to Example 1, except that the catalyst feed is raised from 2.72 mmol/h to 4.85 mmol/h. The results are likewise reproduced in Table 1.
- DETD As Example 1 and Comparative Examples 1 and 2 clearly show, the hydrogen cyanide conversion on using a selectively hydrogenated hydrocarbon mixture is higher than with an unpretreated mixture. Furthermore, Example 1 gives distinctly higher nickel retrieval rates than the comparative examples. The butadiene selectivity is about 1% higher in the process of the invention than in the reference process. Example 1 has less butadiene (excess component) than Comparative Examples 1 and 2. Nonetheless, the conversion of HCN (deficient component) is higher. This effect is surprising, because the conversion of the deficient component should have increased with increasing amount of excess component. Comparative Example 2, which utilizes a distinctly higher catalyst content, still does not match the results of Example 1.
- DETD 4.7 g of catalyst composition containing:
- DETD A glass autoclave is charged with 20.3 g of partially hydrogenated C._{sub.4} cut (corresponding to 7.9 g (0.14 mol) of 1,3-butadiene), 2.75 g of a mixed catalyst (composition: 0.69 g (0.468 mmol) of tetrakis(tri-m-p-tolylphosphite)nickel(0), 1.65 g (4.68 mmol) of tri-m-p-tolylphosphite and 0.41 g 3-pentene nitrile) and 40 g of toluene at room temperature and heated to 90° C., the initial pressure being 4.4 bar. A mixture of 3.2 g (0.117 mol) of freshly distilled hydrogen cyanide in 40 g of toluene is continuously metered in over a period of 100 minutes, whereupon the pressure drops to 3.1 bar. The reaction is then completed by further reacting at 90° C. for another 120 minutes. The course of the reaction is monitored by pressure and temperature measurements. After cooling off, the liquid reaction product is analyzed.
1. A process for preparing mixtures of monoolefinic C._{sub.5} mononitriles having nonconjugated C._{dbd.C} and C._{tbd.N} bonding by catalytic hydrocyanation of a hydrocarbon mixture containing 1,3-butadiene, wherein the hydrocarbon mixture is reacted with hydrogen in the presence of a hydrogenation catalyst capable of hydrogenating alkynes and 1,2-dienes with high selectivity without significantly diminishing the 1,3-butadiene content in order to remove alkynes, 1,2-dienes and mixtures thereof partially or completely so that the proportion of those components in the hydrocarbon mixture which impair the catalytic

hydrocyanation is diminished and then subjecting the resulting mixture to catalytic hydrocyanation.

5. The process of claim 1, wherein the hydrocyanation catalyst catalyzes the position isomerization and double bond isomerization of the hydrocarbon mixture and/or of the nitriles as well as the hydrogen cyanide addition.

7. A process for preparing adiponitrile, which comprises catalytically hydrocyanating a C_{sub}5 mononitrile mixture prepared as claimed in any of claims 1 to 6, optionally after further workup or isomerization.

- IT 106-99-0, Butadiene, reactions
(hydrocyanation in purified C₄ fractions)
- IT 4635-87-4P, 3-Pentenenitrile 16529-56-9P, 2-Methyl-3-butenenitrile
(monoolefinic C₅ mononitrile production and use)
- IT 74-90-8, Hydrocyanic acid, reactions
(reaction with butadiene)
- IT 106-99-0, Butadiene, reactions
(hydrocyanation in purified C₄ fractions)
- RN 106-99-0 USPATFULL
- CN 1,3-Butadiene (CA INDEX NAME)



- IT 4635-87-4P, 3-Pentenenitrile
(monoolefinic C₅ mononitrile production and use)
- RN 4635-87-4 USPATFULL
- CN 3-Pentenenitrile (CA INDEX NAME)



- IT 74-90-8, Hydrocyanic acid, reactions
(reaction with butadiene)
- RN 74-90-8 USPATFULL
- CN Hydrocyanic acid (CA INDEX NAME)



- L88 ANSWER 58 OF 60 USPATFULL on STN
 ACCESSION NUMBER: 1999:1880 USPATFULL Full-text
 TITLE: Process for the hydrocyanation of organic compounds containing ethylenic unsaturation
 INVENTOR(S): Huser, Marc, Villeurbanne, France

PATENT ASSIGNEE(S): Perron, Robert, Charly, France
 Rhone-Poulenc Fiber & Resin Intermediates, Courbevoie
 Cedex, France (non-U.S. corporation)

| PATENT INFORMATION: | NUMBER | KIND | DATE |
|---------------------|----------------|------|--------------|
| | US 5856555 | | 19990105 |
| APPLICATION INFO.: | US 1997-832689 | | 19970411 (8) |

| PRIORITY INFORMATION: | NUMBER | DATE |
|-----------------------|----------------|---------------|
| | FR 1995-11689 | 19950929 |
| | US 1996-15480P | 19960412 (60) |

DOCUMENT TYPE: Utility
 FILE SEGMENT: Granted
 PRIMARY EXAMINER: Richter, Johann
 ASSISTANT EXAMINER: Murray, Joseph
 LEGAL REPRESENTATIVE: Burns, Doane, Swecker & Mathis, L.L.P.
 NUMBER OF CLAIMS: 21
 EXEMPLARY CLAIM: 1
 LINE COUNT: 932

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB The present invention relates to a process for the hydrocyanation of organic compounds containing ethylenic unsaturation to nitrates, in particular the hydrocyanation of diolefins or of substituted olefins, such as alkenenitriles.

More specifically, it comprises a process for the hydrocyanation of organic compounds containing at least one ethylenic double bond by reaction with hydrogen cyanide in the presence of an aqueous solution of a catalyst comprising at least one transition metal compound and at least one water-soluble phosphine, characterized in that the said water-soluble phosphine is a monodentate or bidentate phosphine.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

SUMM . . . alkylene radical, a cycloalkylene radical, an arylene radical or a radical deriving from a heterocycle containing one or two oxygen, nitrogen or sulphur atoms in the ring, these various cyclic radicals being bonded directly to one of the phosphorus atoms or. . .

SUMM . . . diphenylene radical, a naphthylene radical, a dinaphthylene radical or a radical deriving from a heterocycle containing one or two oxygen, nitrogen or sulphur atoms in the ring, these various cyclic radicals being bonded directly to one of the phosphorus atoms or. . .

SUMM . . . is possible, in practice, to charge to a reactor which has been purged beforehand using an inert gas (such as nitrogen or argon) either an aqueous solution containing all or part of the various constituents, such as the water-soluble phosphine, the transition metal.

SUMM It is possible, if appropriate, in this alternative form, to gently sweep the reactor using an inert gas, such as nitrogen or argon, for example, in order to drive off the hydrocyanic acid which could still be present.

DETD . . . of Ni(cyclooctadiene).sub.2, followed by 35 ml of previously degassed ortho-xylene, are subsequently introduced with stirring and under a stream of argon.

DETD . . . of Ni(cyclooctadiene).sub.2, followed by 35 ml of previously degassed ortho-xylene, are subsequently introduced with stirring and under a stream of argon.

DETD . . . of Ni(cyclooctadiene).sub.2, followed by 35 ml of previously degassed ortho-xylene, are subsequently introduced with stirring and under a stream of argon.

DETD . . . of Ni(cyclooctadiene).sub.2, followed by 35 ml of previously degassed ortho-xylene, are subsequently introduced with stirring and under a stream of argon.

DETD . . . of Ni(cyclooctadiene).sub.2, followed by 350 ml of previously degassed ortho-xylene, are subsequently introduced with stirring and under a stream of argon.

CLM What is claimed is:

- · carbon atoms, a phenylene radical, a diphenylene radical or a radical deriving from a heterocycle containing one or two oxygen, nitrogen or sulphur atoms in the ring, these various cyclic radicals being bonded directly to one of the phosphorus atoms or. . .
- · cycloalkylene radical, a phenylene radical, a diphenylene radical and a radical derived from a heterocycle containing one or two oxygen, nitrogen or sulphur atoms in the ring, these various cyclic radicals being bonded directly to one of the phosphorus atoms or. . .

IT 74-90-8, Hydrogen cyanide, reactions 78-79-5, Isoprene, reactions 100-42-5, Styrene, reactions 106-99-0,
 1,3-Butadiene, reactions 110-83-8, Cyclohexene, reactions 111-78-4,
 1,5-Cyclooctadiene 592-42-7, 1,5-Hexadiene 592-51-8, 4-Pentene
 nitrile 1319-73-9, Methylstyrene 1335-86-0, Methylcyclohexene
 4403-61-6, 2-Methyl-2-butene nitrile 4635-87-4, 3-Pentene
 nitrile 13284-42-9, 2-Pentene nitrile 16529-56-9, 2-Methyl-3-butene
 nitrile 26588-32-9, Vinylnaphthalene

(process and water-soluble catalysts for the preparation of nitriles by the hydrocyanation of alkenes and cyanoalkenes)

SUMM L represents a single valency bond or a divalent hydrocarbon radical, such as an alkylene radical, a cycloalkylene radical, an arylene radical or a radical deriving from a heterocycle containing one or two oxygen, nitrogen or sulphur atoms in the ring, these various cyclic radicals being bonded directly to one of the phosphorus atoms or to both phosphorus atoms or being bonded to one of the phosphorus atoms or to both via a linear or branched alkylene radical having from 1 to 4 carbon atoms, it being possible for the ring or rings which are optionally part of the divalent radical L to contain one or a number of substituents, such as an alkyl group having 1 to 4 carbon atoms.

SUMM The preferred water-soluble phosphines are the phosphines of formula (I) or of formula (II) in which Ar1 and Ar2 are phenyl groups or phenyl groups containing one or two substituents as defined above, Ar3 is a phenyl group containing one or two substituents as defined above, D is an alkyl group having from 1 to 6 carbon atoms, a cycloalkyl group having 5 to 8 carbon atoms, an alkyl group having from 1 to 6 carbon atoms containing one or a number of substituents as defined above or a cycloalkyl group having 5 to 8 carbon atoms containing one or a number of substituents as defined above and L is a single valency bond, an alkylene radical having from 1 to 6 carbon atoms, a monocyclic or bicyclic cycloalkylene radical having from 4 to 12 carbon atoms, a phenylene radical, a diphenylene radical, a naphthylene radical, a dinaphthylene radical or a radical deriving from a heterocycle containing one or two oxygen, nitrogen or sulphur atoms in the ring, these various cyclic radicals being bonded directly to one of the phosphorus atoms or to both phosphorus atoms or being bonded to one of the phosphorus atoms or to both via a linear or branched alkylene radical having from 1 to 4 carbon atoms, it being possible for the ring or rings which are optionally part of the divalent radical L to contain one or a number of substituents, such as an alkyl group having 1 to 4 carbon atoms.

- SUMM Within the context of a batchwise implementation, it is possible, in practice, to charge to a reactor which has been purged beforehand using an inert gas (such as nitrogen or argon) either an aqueous solution containing all or part of the various constituents, such as the water-soluble phosphine, the transition metal compound, the possible reducing agent and the possible solvent, or the said constituents separately. Generally, the reactor is then brought to the chosen temperature and then the pentenenitrile is introduced. The hydrogen cyanide is then itself introduced, preferably continuously and uniformly.
- SUMM It is possible, if appropriate, in this alternative form, to gently sweep the reactor using an inert gas, such as nitrogen or argon, for example, in order to drive off the hydrocyanic acid which could still be present.
- DETD 50 ml of a solution of 11.3 mmol of sodium salt of 1,2-bis[di(sulphonatophenyl)phosphinomethyl]-cyclobutane (CBDTsNa._{sub.4}) in water are charged to a 100 ml round-bottomed glass flask equipped with a magnetic bar and an ascending reflux condenser; this solution is degassed. 2 g (7.3 mmol) of Ni(cyclooctadiene)._{sub.2}, followed by 35 ml of previously degassed ortho-xylene, are subsequently introduced with stirring and under a stream of argon.
- DETD 50 ml of a solution of 32.8 mmol of sodium salt of tris(para-phosphophenyl)phosphine (TPPPNa._{sub.6}) in water are charged to a 100 ml round-bottomed glass flask equipped with a magnetic bar and an ascending reflux condenser; this solution is degassed. 2 g (7.3 mmol) of Ni(cyclooctadiene)._{sub.2}, followed by 35 ml of previously degassed ortho-xylene, are subsequently introduced with stirring and under a stream of argon.
- DETD 50 ml of a solution of 32.8 mmol of sodium salt of bis(meta-sulphophenyl)(para-carboxyphenyl)-phosphine (DSPCPNa._{sub.3}) in water are charged to a 100 ml round-bottomed glass flask equipped with a magnetic bar and an ascending reflux condenser; this solution is degassed. 2 g (7.3 mmol) of Ni(cyclooctadiene)._{sub.2}, followed by 35 ml of previously degassed ortho-xylene, are subsequently introduced with stirring and under a stream of argon.
- DETD 50 ml of a solution of 32.8 mmol of sodium salt of bis(meta-sulphophenyl)(2-sulphoethyl)phosphine (DSPSEPNa._{sub.3}) in water are charged to a 100 ml round-bottomed glass flask equipped with a magnetic bar and an ascending reflux condenser; this solution is degassed. 2 g (7.3 mmol) of Ni(cyclooctadiene)._{sub.2}, followed by 35 ml of previously degassed ortho-xylene, are subsequently introduced with stirring and under a stream of argon.
- DETD 500 ml of a solution of 300 mmol of sodium salt of tris(meta-sulphophenyl)phosphine (TPFTsNa._{sub.3}) in water are charged to a 1000 ml round-bottomed glass flask equipped with a stirrer and an ascending reflux condenser; this solution is degassed. 20 g (73 mmol) of Ni(cyclooctadiene)._{sub.2}, followed by 350 ml of previously degassed ortho-xylene, are subsequently introduced with stirring and under a stream of argon.
2. The process according to claim 1, wherein the water-soluble phosphines are the phosphines of formula (I) or of formula (II) in which Ar1 and Ar2 are phenyl groups or phenyl groups containing one or two substituents, Ar3 is a phenyl group containing one or two substituents, D is an alkyl group having from 1 to 6 carbon atoms, a cycloalkyl group having 5 to 8 carbon atoms, an alkyl group having from 1 to 6 carbon atoms containing one or a number of substituents or a cycloalkyl group having 5 to 8 carbon atoms containing one or a number of substituents

and L is a single valency bond, an alkylene radical having from 1 to 6 carbon atoms, a monocyclic or bicyclic cycloalkylene radical having from 4 to 12 carbon atoms, a phenylene radical, a diphenylene radical or a radical deriving from a heterocycle containing one or two oxygen, nitrogen or sulphur atoms in the ring, these various cyclic radicals being bonded directly to one of the phosphorus atoms or to both phosphorus atoms or being bonded to one of the phosphorus atoms or to both via a linear or branched alkylene radical having from 1 to 4 carbon atoms, it being possible for the ring or rings which are optionally part of the divalent radical L to contain one or a number of substituents.

21. The process of claim 1, wherein said water-soluble phosphine is a monodentate or bidentate phosphine corresponding to the general formula (II) in which L is a divalent hydrocarbon radical selected from the group consisting of an alkylene radical, a cycloalkylene radical, a phenylene radical, a diphenylene radical and a radical derived from a heterocycle containing one or two oxygen, nitrogen or sulphur atoms in the ring, these various cyclic radicals being bonded directly to one of the phosphorus atoms or to both phosphorus atoms or being bonded to one of the phosphorus atoms or to both via a linear or branched alkylene radical having from 1 to 4 carbon atoms, it being possible for the ring or rings which are optionally part of the divalent radical L to contain one or a number of substituents.

- IT 74-90-8, Hydrogen cyanide, reactions 78-79-5, Isoprene, reactions 100-42-5, Styrene, reactions 106-99-0,
 1,3-Butadiene, reactions 110-83-8, Cyclohexene, reactions 111-78-4,
 1,5-Cyclooctadiene 592-42-7, 1,5-Hexadiene 592-51-8, 4-Pentene
 nitrile 1319-73-9, Methylstyrene 1335-86-0, Methylcyclohexene
 4403-61-6, 2-Methyl-2-butene nitrile 4635-87-4, 3-Pentene
 nitrile 13284-42-9, 2-Pentene nitrile 16529-56-9, 2-Methyl-3-butene
 nitrile 26588-32-9, Vinylnaphthalene
 (process and water-soluble catalysts for the preparation of nitriles by the
 hydrocyanation of alkenes and cyanoalkenes)
 IT 74-90-8, Hydrogen cyanide, reactions 106-99-0,
 1,3-Butadiene, reactions 4635-87-4, 3-Pentene nitrile
 (process and water-soluble catalysts for the preparation of nitriles by the
 hydrocyanation of alkenes and cyanoalkenes)
 RN 74-90-8 USPATFULL
 CN Hydrocyanic acid (CA INDEX NAME)



- RN 106-99-0 USPATFULL
 CN 1,3-Butadiene (CA INDEX NAME)



- RN 4635-87-4 USPATFULL
 CN 3-Pentenenitrile (CA INDEX NAME)



L88 ANSWER 59 OF 60 USPATFULL on STN

ACCESSION . . .

are converted to nitriles by reacting with hydrogen cyanide in the presence of an organic thiol or sulphide and a catalytic amount of a cuprous salt which is soluble therein; especially for making 3-pentene nitrile from butadiene.

CAS INDEXING IS AVAILABLE. . .

AB . . . are converted to nitriles by reacting with hydrogen cyanide in the presence of an organic thiol or sulphide and a catalytic amount of a cuprous salt which is soluble therein; especially for making 3-pentene nitrile from butadiene.

SUMM . . . nitriles and, more particularly, to their manufacture by reaction of olefinic compounds with hydrogen cyanide in the presence of a catalyst.

SUMM . . . nitriles which comprises reacting an olefin with hydrogen cyanide in the presence of an organic thiol or sulphide and a catalytic amount of a cuprous salt which is soluble in the said thiol or sulphide.

SUMM . . . unsaturation. Moreover, the heterocyclic rings containing the S atom may contain carbon-carbon unsaturation and may contain other hetero atoms, especially nitrogen, oxygen or sulphur atoms. Preferably the heterocyclic rings have 5, 6 or 7, especially 5 or 6, atoms in the. . .

SUMM . . . may be carried out over a wide range of temperatures, for example from -25° to 200°C. Because of decay of catalyst at higher temperatures, however, and because of the low rate of reaction at lower temperatures it preferred to operate in. . .

SUMM . . . range of olefin to hydrogen cyanide of 2 : 1 to 1 : 10. The cuprous salt is used in catalytic amount: this will normally fall within the range 0.0005 to 0.1 mole per mole of olefin. We prefer that the. . .

SUMM . . . hydrogen cyanide in the presence of, for example, cuprous chloride, to give 3-pentene nitrile. Although the reaction is described as catalytic good yields of 3-pentene nitrile are obtained only if substantially equimolar proportions of butadiene and cuprous salt are used. With catalytic proportions, for example 0.006 moles of cuprous chloride per mole of butadiene, both the conversion of butadiene and the yield of 3-pentene nitrile are low. In the process of our invention, however, catalytic amounts of cuprous salt, when used in conjunction with an organic thiol or sulphide, give good conversions of butadiene and. . .

SUMM It has already been proposed to react butadiene and hydrogen cyanide in the presence of catalytic amounts of certain catalysts, for example certain zerovalent nickel catalysts, as described, for example, in United Kingdom patent specification No. 1,104,140. Such processes give mixtures of linear pentene nitriles, which. . . is the ratio of 3-pentene nitrile to branched methyl butenonitriles is at least 4 : 1. Moreover, the zero-valent nickel catalysts used in the prior process are sensitive to moisture whereas the catalysts used in the process of our present invention are not. Thus, anhydrous conditions are not required and it is not. . .

SUMM 3-Pentene nitrile is particularly valuable for further reaction with hydrogen cyanide in the presence of a catalyst to give adiponitrile.

Adiponitrile may be hydrogenated to hexamethylene diamine, a valuable intermediate for polycondensation with dicarboxylic acids to give. . . . ml. of di-n-propyl sulphide (or the compound specified in the Table) and the solution introduced into a tube filled with nitrogen. After purging with nitrogen, 5 ml. of hydrogen cyanide, redistilled from phosphorus pentoxide, were condensed into the tube at -78°C. 10 ml. of butadiene, . . . cooled to -78°C and opened.

Unreacted butadiene and hydrogen cyanide were distilled off and the remaining liquor filtered from solid catalyst. The liquor was then analysed by gas-liquid chromatography for 3-pentene nitrile 2-methyl-3-butene nitrile and adiponitrile.

DETD Anhydrous cuprous chloride (0.6 g.) was dissolved in 1 ml. of di-n-propyl sulphide in a tube filled with nitrogen and 8.2 g. of isoprene were introduced. After purging with nitrogen, 5 ml. of hydrogen cyanide, distilled from phosphorus pentoxide, were introduced and the tube sealed. The mixture was then stirred. . . . ml. of hydrogen cyanide, and heating was continued for 20 hours at 140°C, the liquid product was filtered from solid catalyst and distilled to give 4.93 g. of 4-methyl-3-pentenenitrile, b.pt. 158°-162°C of greater than 97% purity. The conversion of isoprene was. . . .

IT 74-90-8
(addition reaction of, with butadiene and isoprene, catalysts for)

IT 78-79-5, reactions 106-39-0, reactions
(addition reaction of, with hydrocyanic acid, catalysts for)

IT 4635-67-4P 16529-56-9P
(from butadiene by reaction with hydrocyanic acid, catalysts for)

PI US 3947487 19760330 <--

AB Olefins are converted to nitriles by reacting with hydrogen cyanide in the presence of an organic thiol or sulphide and a catalytic amount of a cuprous salt which is soluble therein; especially for making 3-pentene nitrile from butadiene.

SUMM This invention relates to the manufacture of organic nitriles and, more particularly, to their manufacture by reaction of olefinic compounds with hydrogen cyanide in the presence of a catalyst.

SUMM Our invention provides a process for the manufacture of organic nitriles which comprises reacting an olefin with hydrogen cyanide in the presence of an organic thiol or sulphide and a catalytic amount of a cuprous salt which is soluble in the said thiol or sulphide.

SUMM in which R.sub.1 and R.sub.2 are aliphatic, cycloaliphatic, araliphatic or aromatic radicals, and, in the case of sulphides, may be the same or different, and may be joined to form, with the S atom, a heterocyclic ring containing sulphur. The radicals R.sub.1 and R.sub.2 may carry substituents, for example hydroxyl, alkoxyl, carboxylic ester and halogen substituents, and the aliphatic and cycloaliphatic radicals they represent may contain carbon-carbon unsaturation, especially ethylene unsaturation. Moreover, the heterocyclic rings containing the S atom may contain carbon-carbon unsaturation and may contain other hetero atoms, especially nitrogen, oxygen or sulphur atoms. Preferably the heterocyclic rings have 5, 6 or 7, especially 5 or 6, atoms in the ring.

SUMM The process of our invention may be carried out over a wide range of temperatures, for example from -25° to 200°C. Because of decay of catalyst at higher temperatures, however, and because of the low rate of reaction at lower temperatures it preferred to operate in the temperature range 50° to 160°C, and more preferably from 90° to 135°C, temperatures of about 120°C

being very suitable. Owing to the volatility and toxicity of hydrogen cyanide the reaction is preferably conducted in a closed vessel under autogenous pressure or, if desired, under deliberately raised pressure, for example at a pressure of from 1 to 50 atmospheres. If desired a solvent may be used, for example a hydrocarbon solvent such as benzene, toluene or xylene or a nitrile solvent such as acetonitrile, propionitrile, benzonitrile or adiponitrile. Agitation of the reactants is desirable. The reaction is continued for a time sufficient to give a suitable conversion. In the case of a batch process the time will normally be for from 1 hour up to a period of several days, for example 5 days.

SUMM The olefin and the hydrogen cyanide may be used in equimolar proportions or an excess of either may be used, especially within the molar range of olefin to hydrogen cyanide of 2 : 1 to 1 : 10. The cuprous salt is used in catalytic amount: this will normally fall within the range 0.0005 to 0.1 mole per mole of olefin. We prefer that the proportion of the said salt is from 0.005 to 0.05 mole per mole of olefine.

SUMM U.S. Pat. No. 2,509,859 describes the reaction of butadiene and hydrogen cyanide in the presence of, for example, cuprous chloride, to give 3-pentene nitrile. Although the reaction is described as catalytic good yields of 3-pentene nitrile are obtained only if substantially equimolar proportions of butadiene and cuprous salt are used. With catalytic proportions, for example 0.006 moles of cuprous chloride per mole of butadiene, both the conversion of butadiene and the yield of 3-pentene nitrile are low. In the process of our invention, however, catalytic amounts of cuprous salt, when used in conjunction with an organic thiol or sulphide, give good conversions of butadiene and good yields of 3-pentene nitrile.

SUMM It has already been proposed to react butadiene and hydrogen cyanide in the presence of catalytic amounts of certain catalysts, for example certain zerovalent nickel catalysts, as described, for example, in United Kingdom patent specification No. 1,104,140. Such processes give mixtures of linear pentene nitriles, which are convertible by further reaction with hydrogen cyanide into adiponitrile, and branched methyl butene nitriles which cannot be converted directly into adiponitrile. The proportion of linear pentene nitriles compared with branched methyl butene nitriles produced in such processes is not normally greatly in excess of 70% by weight (or molar). It is an advantage of the process of our invention that the proportion of linear 3-pentene nitrile, directly convertible to adiponitrile, which is produced is much higher, usually at least 80% by weight (or molar), that is the ratio of 3-pentene nitrile to branched methyl butenenitriles is at least 4 : 1. Moreover, the zero-valent nickel catalysts used in the prior process are sensitive to moisture whereas the catalysts used in the process of our present invention are not. Thus, anhydrous conditions are not required and it is not therefore necessary, for example, to specially dry the olefin and hydrogen cyanide.

SUMM 3-Pentene nitrile is particularly valuable for further reaction with hydrogen cyanide in the presence of a catalyst to give adiponitrile. Adiponitrile may be hydrogenated to hexamethylene diamine, a valuable intermediate for polycondensation with dicarboxylic acids to give polyamides, especially, for example, with adipic acid to give polyhexamethylene adipamide (nylon 6,6), a well-known polyamide for use in the manufacture of mouldings and for melt spinning into synthetic fibres.

DETD Anhydrous cuprous chloride (0.6 g.) was dissolved in 0.9 ml. of di-n-propyl sulphide (or the compound specified in the Table) and the solution introduced into a tube filled with nitrogen. After purging with nitrogen, 5 ml. of hydrogen cyanide, redistilled from phosphorus pentoxide, were condensed into the tube at -78°C. 10 ml. of butadiene, purified by passage through an ion exchange column, were then distilled into the tube which was then sealed. The mixture was then stirred magnetically and heated to the operating temperature for the operating period (see Table). The tube was then cooled to -78°C and opened. Unreacted butadiene and hydrogen cyanide were distilled off and the remaining liquor filtered from solid catalyst. The liquor was then analysed by gas-liquid chromatography for 3-pentene nitrile 2-methyl-3-butene nitrile and adiponitrile.

DETD Anhydrous cuprous chloride (0.6 g.) was dissolved in 1 ml. of di-n-propyl sulphide in a tube filled with nitrogen and 8.2 g. of isoprene were introduced. After purging with nitrogen, 5 ml. of hydrogen cyanide, distilled from phosphorus pentoxide, were introduced and the tube sealed. The mixture was then stirred magnetically and heated at 110°C for 17 hours. After cooling, the tube was opened, excess volatile material distilled off and the residue distilled to give 8.2 g. of mononitriles (71.7% conversion of isoprene), over 95% of which was 4-methyl-3-pentenenitrile.

DETD In an experiment conducted similarly to that in Example 4 except that the reactants were 0.6 g. of anhydrous cuprous chloride, 1 g. of dibenzyl sulphide, 8 g. of isoprene and 5 ml. of hydrogen cyanide, and heating was continued for 20 hours at 140°C, the liquid product was filtered from solid catalyst and distilled to give 4.93 g. of 4-methyl-3-pentenenitrile, b.pt. 158°-162°C of greater than 97% purity. The conversion of isoprene was 44.1%.

IT 74-90-8
 (addition reaction of, with butadiene and isoprene, catalysts for)

IT 78-79-5, reactions 106-99-0, reactions
 (addition reaction of, with hydrocyanic acid, catalysts for)

IT 4635-87-4P 16529-56-9P
 (from butadiene by reaction with hydrocyanic acid, catalysts for)

IT 74-90-8
 (addition reaction of, with butadiene and isoprene, catalysts for)

RN 74-90-8 USPATFULL

CN Hydrocyanic acid (CA INDEX NAME)



IT 106-99-0, reactions
 (addition reaction of, with hydrocyanic acid, catalysts for)

RN 106-99-0 USPATFULL

CN 1,3-Butadiene (CA INDEX NAME)



IT 4635-87-4P

(from butadiene by reaction with hydrocyanic acid, catalysts for)
 RN 4635-87-4 USPATFULL
 CN 3-Pentenenitrile (CA INDEX NAME)



L88 ANSWER 60 OF 60 USPATFULL on STN

ACCESSION . . .

THIS PATENT.

- AB Organic nitriles are obtained by reaction of an olefin and hydrogen cyanide in the presence of a catalytic amount of a Group IB metal salt, especially a cuprous halide and an organic acid. With butadiene as the olefin. . .
- AB Organic nitriles are obtained by reaction of an olefin and hydrogen cyanide in the presence of a catalytic amount of a Group IB metal salt, especially a cuprous halide and an organic acid. With butadiene as the olefin. . .
- SUMM . . . nitriles and, more particularly, to their manufacture by reaction of olefinic compounds with hydrogen cyanide in the presence of a catalyst.
- SUMM . . . Group IB of the Periodic System, for example cuprous chloride, to give 3-pentene nitrile. Although the reaction is described as catalytic good yields of 3-pentene nitrile are obtained only if substantially equimolar proportions of butadiene and Group IB metal halide are used. With catalytic proportions, for example 0.006 moles of cuprous chloride per mole of butadiene, both the conversion of butadiene and the yield. . .
- SUMM We have now found that good yields of product are obtained using only catalytic amounts of Group IB metal salt if the said salt is used in conjunction with an organic acid.
- SUMM . . . process for the manufacture of organic nitriles which comprises reacting an olefin with hydrogen cyanide in the presence of a catalytic amount of a Group IB metal salt and an organic acid.
- SUMM . . . normally be for from 1 hour up to a period of several days, for example 5 days. If a supported catalyst is used the time of contact could be as low as a few seconds, for example 3 seconds.
- SUMM . . . the molar range of olefin to hydrogen cyanide of 2:1 to 1:4. The Group IB metal salt is used in catalytic amount: this will normally fall within the range 0.0005 to 0.1 moles per mole of olefin. We prefer that the. . .
- SUMM . . . olefin and/or hydrogen cyanide by distillation or by simply venting the apparatus. The organic nitrile may then be separated from catalyst residues by conventional methods such as filtration with or without extraction with solvent, or by distillation. The process may readily. . .
- SUMM . . . Specification No. 2,509,859 the process of our invention enables the conversion to be effected in good yield using only a catalytic amount of Group IB metal halide, in conjunction with the organic acid instead of the equimolar amount required by the. . .
- SUMM 3-Pentene nitrile is particularly valuable for further reaction with hydrogen cyanide in the presence of catalyst to give adiponitrile. Adiponitrile may be hydrogenated to hexamethylene diamine, a valuable intermediate for polycondensation with dicarboxylic acids to give. . .
- SUMM It has already been proposed to react butadiene and hydrogen cyanide in the presence of catalytic amounts of certain catalysts, for example certain zero valent nickel catalysts, as described, for example, in United Kingdom Specification No. 1,104,140. Such processes give mixtures

of linear pentene nitriles, which are. . . adiponitrile, which is produced is much higher, usually at least 80% by weight (or molar). Moreover, the zero valent nickel catalyst used in the prior process are sensitive to moisture whereas the catalysts used in our process are not. Thus, anhydrous conditions are not required and it is not, therefore, necessary, for example, . . .

CLM What is claimed is:

- . . molar ratio 2:1 to 1:4 at a temperature within the range -25° to 200°C in the presence, as a sole catalyst, of from 0.0005 to 0.1 moles per mole of butadiene of cuprous chloride, bromide or iodide and a carboxylic acid. . .

IT 4635-87-4P

(preparation of)

IT 74-90-8

(reaction of, with butadiene)

IT 106-99-0, reactions

(with hydrocyanic acid)

PI US 3869501

19750304

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AB Organic nitriles are obtained by reaction of an olefin and hydrogen cyanide in the presence of a catalytic amount of a Group IB metal salt, especially a cuprous halide and an organic acid. With butadiene as the olefin the nitrile product contains more than 80% by weight of linear 3-pentene nitrile.|

SUMM This invention relates to the manufacture of organic nitriles and, more particularly, to their manufacture by reaction of olefinic compounds with hydrogen cyanide in the presence of a catalyst.

SUMM United States Patent Specification No. 2,509,859 describes the reaction of butadiene and hydrogen cyanide in the presence of a halide of a metal of Group IB of the Periodic System, for example cuprous chloride, to give 3-pentene nitrile. Although the reaction is described as catalytic good yields of 3-pentene nitrile are obtained only if substantially equimolar proportions of butadiene and Group IB metal halide are used. With catalytic proportions, for example 0.006 moles of cuprous chloride per mole of butadiene, both the conversion of butadiene and the yield of 3-pentene nitrile are low.

SUMM We have now found that good yields of product are obtained using only catalytic amounts of Group IB metal salt if the said salt is used in conjunction with an organic acid.

SUMM Accordingly our invention provides a process for the manufacture of organic nitriles which comprises reacting an olefin with hydrogen cyanide in the presence of a catalytic amount of a Group IB metal salt and an organic acid.

SUMM The process of our invention may be carried out over a wide range of temperatures, for example from -25° to 200°C, preferably from 20° to 150°C, and more preferably from 50° to 120°C. Owing to the volatility and toxicity of hydrogen cyanide the reaction is preferably conducted in a closed vessel under autogenous pressure or, if desired, under deliberately raised pressure, for example at a pressure of from 1 to 50 atmospheres. If desired a solvent may be used, for example a hydrocarbon solvent such as benzene, toluene or xylene or a nitrile solvent such as acetonitrile, propionitrile, benzonitrile or adiponitrile. Agitation of the reactants is desirable. The reaction is continued for a time sufficient to give a suitable conversion. In the case of a batch process the time will normally be for from 1 hour up to a period of several days, for example 5 days. If a supported catalyst is used the time of contact could be as low as a

few seconds, for example 3 seconds.

SUMM The olefin and the hydrogen cyanide may be used in equimolar proportions or an excess of either may be used, especially within the molar range of olefin to hydrogen cyanide of 2:1 to 1:4. The Group IB metal salt is used in catalytic amount: this will normally fall within the range 0.0005 to 0.1 moles per mole of olefin. We prefer that the proportion of the said salt is from 0.005 to 0.05 moles per mole of olefin.

SUMM The organic nitrile formed in the process may be separated from the reaction mixture by first removing any excess olefin and/or hydrogen cyanide by distillation or by simply venting the apparatus. The organic nitrile may then be separated from catalyst residues by conventional methods such as filtration with or without extraction with solvent, or by distillation. The process may readily be adapted to continuous operation.

SUMM The process of our invention is particularly valuable for the conversion of butadiene to 3-pentene nitrile. Compared with the process of United States Patent Specification No. 2,509,859 the process of our invention enables the conversion to be effected in good yield using only a catalytic amount of Group IB metal halide, in conjunction with the organic acid instead of the equimolar amount required by the prior process.

SUMM 3-Pentene nitrile is particularly valuable for further reaction with hydrogen cyanide in the presence of a catalyst to give adiponitrile. Adiponitrile may be hydrogenated to hexamethylene diamine, a valuable intermediate for polycondensation with dicarboxylic acids to give polyamides, especially, for example, with adipic acid to give polyhexamethylene adipamide (nylon 6,6), a well-known polyamide for use in the manufacture of mouldings and for melt spinning into synthetic fibres.

SUMM It has already been proposed to react butadiene and hydrogen cyanide in the presence of catalytic amounts of certain catalysts, for example certain zero valent nickel catalysts, as described, for example, in United Kingdom Specification No. 1,104,140. Such processes give mixtures of linear pentene nitriles, which are convertible by further reaction with hydrogen cyanide into adiponitrile, and branched methylbutene nitriles which cannot be converted directly to adiponitrile. The proportion of linear pentene nitriles compared with branched methylbutene nitriles produced in such processes is not normally greatly in excess of 70% by weight (or molar). It is an advantage of the process for our invention that the proportion of linear 3-pentene nitrile, directly convertible to adiponitrile, which is produced is much higher, usually at least 80% by weight (or molar). Moreover, the zero valent nickel catalysts used in the prior process are sensitive to moisture whereas the catalysts used in our process are not. Thus, anhydrous conditions are not required and it is not, therefore, necessary, for example, to specially dry the olefin and hydrogen cyanide.

1. A process for the manufacture of 3-pentene nitrile which comprises reacting butadiene with hydrogen cyanide in the molar ratio 2:1 to 1:4 at a temperature within the range -25° to 200°C in the presence, as a sole catalyst, of from 0.0005 to 0.1 moles per mole of butadiene of cuprous chloride, bromide or iodide and a carboxylic acid selected from benzoic acid, oxalic acid and compounds having one or two carboxylic acid groups attached to a saturated or ethylenically unsaturated hydrocarbon residue containing up to three carbon atoms and

10/586490

IT 4635-87-4P
(preparation of)
IT 74-90-8
(reaction of, with butadiene)
IT 106-99-0, reactions
(with hydrocyanic acid)
IT 4635-87-1P
(preparation of)
RN 4635-87-4 USPATFULL
CN 3-Pentenenitrile (CA INDEX NAME)



IT 74-90-8
(reaction of, with butadiene)
RN 74-90-8 USPATFULL
CN Hydrocyanic acid (CA INDEX NAME)



IT 106-99-0, reactions
(with hydrocyanic acid)
RN 106-99-0 USPATFULL
CN 1,3-Butadiene (CA INDEX NAME)



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(FILE 'HOME' ENTERED AT 14:42:47 ON 01 FEB 2008)

FILE 'ZCAPLUS' ENTERED AT 14:43:01 ON 01 FEB 2008

FILE 'CPLUS' ENTERED AT 14:43:07 ON 01 FEB 2008
E US2006-586490/APPS

L1 1 SEA ABB=ON PLU=ON US2006-586490/AP
D SCA

FILE 'REGISTRY' ENTERED AT 14:44:22 ON 01 FEB 2008

L2 1 SEA ABB=ON PLU=ON 4635-87-4
L3 1 SEA ABB=ON PLU=ON 16529-56-9
L4 1 SEA ABB=ON PLU=ON 74-90-8
L5 1 SEA ABB=ON PLU=ON 106-99-0
D SCA
D SCA L3
D SCA L2
L6 2248 SEA ABB=ON PLU=ON PENTENENITRILE/CNS
L7 136 SEA ABB=ON PLU=ON L6 AND 5/C
L8 64 SEA ABB=ON PLU=ON L7 AND STEREOSEARCH/FS
E 3-PENTENENITRILE,
(3E)-/CN
L9 2 SEA ABB=ON PLU=ON "3-PENTENENITRILE, ("?/CN
D SCA L2
L10 3 SEA ABB=ON PLU=ON L2 OR L9
SEL RN
L11 2 SEA ABB=ON PLU=ON (16529-66-1/CRN OR 16545-78-1/CRN OR
4635-87-4/CRN)
D SCA
L12 465 SEA ABB=ON PLU=ON 3-PENTENENITRILE/CNS
L13 5 SEA ABB=ON PLU=ON L10 OR L11
L14 460 SEA ABB=ON PLU=ON L12 NOT L13
L15 432 SEA ABB=ON PLU=ON L14 AND NC<2
L16 34 SEA ABB=ON PLU=ON L15 AND 5/C
D SCA
E "3-PENTENENITRILE-2,2-D2 "/CN
E "3-PENTENENITRILE-2,2-D2"/CN
L17 1 SEA ABB=ON PLU=ON "3-PENTENENITRILE-2,2-D2"/CN
L18 6 SEA ABB=ON PLU=ON L13 OR L17
D SCA
L19 1 SEA ABB=ON PLU=ON L18 AND NC>2
D SCA

FILE 'ZCAPLUS' ENTERED AT 14:56:54 ON 01 FEB 2008

FILE 'CPLUS' ENTERED AT 14:56:59 ON 01 FEB 2008

L*** DEL 830 S L!9
L20 0 SEA ABB=ON PLU=ON L19

FILE 'REGISTRY' ENTERED AT 14:57:20 ON 01 FEB 2008
D LC L19

FILE 'CPLUS' ENTERED AT 14:57:21 ON 01 FEB 2008

FILE 'REGISTRY' ENTERED AT 14:57:44 ON 01 FEB 2008
D ED L19

10/586490

FILE 'CAPLUS' ENTERED AT 14:57:44 ON 01 FEB 2008

FILE 'REGISTRY' ENTERED AT 14:58:09 ON 01 FEB 2008
D SCA L3
D SCA L4
D SCA L5

FILE 'CAPLUS' ENTERED AT 14:58:30 ON 01 FEB 2008

L21 17208 SEA ABB=ON PLU=ON L4
L22 24982 SEA ABB=ON PLU=ON L5
L23 383 SEA ABB=ON PLU=ON L18
L24 47 SEA ABB=ON PLU=ON L21 AND L22 AND L23
L25 130 SEA ABB=ON PLU=ON L18 (L) PREP/RL
L26 3070185 SEA ABB=ON PLU=ON (RACT OR RCT OR RGT) /RL
L27 2588 SEA ABB=ON PLU=ON L21 (L) L26
L28 9152 SEA ABB=ON PLU=ON L22 (L) L26
L29 32 SEA ABB=ON PLU=ON L27 AND L28 AND L25
L30 297092 SEA ABB=ON PLU=ON ?POROUS?/BI
L31 40403 SEA ABB=ON PLU=ON MICROPOR?/BI
 E MOLECULAR SIEVES+ALL/CT
L32 30953 SEA ABB=ON PLU=ON MOLECULAR SIEV?/BI
L33 128603 SEA ABB=ON PLU=ON ZEOLIT?/BI
L34 23369 SEA ABB=ON PLU=ON MESOPOR?/BI
L35 1378 SEA ABB=ON PLU=ON ADSORBANT?/BI
L36 375297 SEA ABB=ON PLU=ON CERAMIC?/BI
L37 54059 SEA ABB=ON PLU=ON AIR/CT
 E NOBLE GASES+ALL/CT
L38 18350 SEA ABB=ON PLU=ON NOBLE GAS?/BI
L39 15276 SEA ABB=ON PLU=ON HELIUM GROUP?/BI
L40 1 SEA ABB=ON PLU=ON L29 AND (L30 OR L31 OR L32 OR L33 OR L34
 OR L35 OR L36)
 D SCA
L41 1 SEA ABB=ON PLU=ON L29 AND (L37 OR L38 OR L39)
 D SCA
L42 2 SEA ABB=ON PLU=ON L24 AND (L30 OR L31 OR L32 OR L33 OR L34
 OR L35 OR L36 OR L37 OR L38 OR L39)
 D SCA

FILE 'USPATFULL' ENTERED AT 15:09:13 ON 01 FEB 2008

L43 24 SEA ABB=ON PLU=ON L4 AND L5 AND L18
L44 6 SEA ABB=ON PLU=ON L43 AND (L30 OR L31 OR L32 OR L33 OR L34
 OR L35 OR L36)
L45 2 SEA ABB=ON PLU=ON L43 AND (L37 OR L38 OR L39)
L46 1 SEA ABB=ON PLU=ON L44 AND L45
L47 250630 SEA ABB=ON PLU=ON HELIUM OR ARGON OR NEON OR KRYPTON OR
 XENON OR RADON
L48 14 SEA ABB=ON PLU=ON L47 AND L43
 D KWIC 1-4
L49 4 SEA ABB=ON PLU=ON L44 AND L47
L50 1664593 SEA ABB=ON PLU=ON AIR OR NITROGEN
L51 15 SEA ABB=ON PLU=ON L43 AND L50
L52 19 SEA ABB=ON PLU=ON L48 OR L51
L53 485246 SEA ABB=ON PLU=ON CATALY?
L54 24 SEA ABB=ON PLU=ON L43 AND L53

FILE 'CAPLUS' ENTERED AT 15:13:52 ON 01 FEB 2008

L55 TRA PLU=ON L25 1- PN : 646 TERMS

FILE 'USPATFULL' ENTERED AT 15:13:59 ON 01 FEB 2008

L56 56 SEA ABB=ON PLU=ON L55

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L57 18 SEA ABB=ON PLU=ON L56 AND L54
L58 1664602 SEA ABB=ON PLU=ON L44 OR L45 OR L48 OR L50 OR L57
L59 24 SEA ABB=ON PLU=ON L44 OR L45 OR L48 OR L51 OR L57

FILE 'CAPLUS' ENTERED AT 15:15:58 ON 01 FEB 2008

FILE 'REGISTRY' ENTERED AT 15:16:33 ON 01 FEB 2008
L60 1 SEA ABB=ON PLU=ON 1344-28-1
D SCA

FILE 'CAPLUS' ENTERED AT 15:16:46 ON 01 FEB 2008
L61 4 SEA ABB=ON PLU=ON L60 AND L24
E ALUMINA/CT
E ALUMINA+ALL/CT
L62 314410 SEA ABB=ON PLU=ON ALUMINA/BI
L63 4 SEA ABB=ON PLU=ON L24 AND L62
L64 1462878 SEA ABB=ON PLU=ON ?CATALY?/BI
L65 43 SEA ABB=ON PLU=ON L64 AND L24
L66 32 SEA ABB=ON PLU=ON L64 AND L29
L67 33 SEA ABB=ON PLU=ON L40 OR L41 OR L42 OR L61 OR L63 OR L66

FILE 'CASREACT' ENTERED AT 15:20:52 ON 01 FEB 2008
L68 39 SEA ABB=ON PLU=ON L18/PRO
D QUE L4
L69 723 SEA ABB=ON PLU=ON 74-90-8
D QUE L5
L70 1995 SEA ABB=ON PLU=ON 106-99-0
L71 16 SEA ABB=ON PLU=ON L68 (L) L69
L72 15 SEA ABB=ON PLU=ON L71 (L) L70
D SCA

FILE 'CAPLUS' ENTERED AT 15:24:40 ON 01 FEB 2008
L73 15 SEA ABB=ON PLU=ON L72
L74 12 SEA ABB=ON PLU=ON L73 AND L24
L75 3 SEA ABB=ON PLU=ON L73 NOT L74
D SCA
SEL AN

FILE 'REGISTRY' ENTERED AT 15:29:29 ON 01 FEB 2008
L76 1 SEA ABB=ON PLU=ON NITROGEN/CN
L77 1 SEA ABB=ON PLU=ON HELIUM/CN
L78 1 SEA ABB=ON PLU=ON ARGON/CN
L79 1 SEA ABB=ON PLU=ON KRYPTON/CN
L80 1 SEA ABB=ON PLU=ON NEON/CN
L81 1 SEA ABB=ON PLU=ON XENON/CN
L82 1 SEA ABB=ON PLU=ON RADON/CN
L83 1 SEA ABB=ON PLU=ON AIR/CN
L*** DEL 0 S L24 AND L76-L83

FILE 'CAPLUS' ENTERED AT 15:31:03 ON 01 FEB 2008
L84 2 SEA ABB=ON PLU=ON L24 AND (L76 OR L77 OR L78 OR L79 OR L80
OR L81 OR L82 OR L83)
L85 0 SEA ABB=ON PLU=ON L75 AND (L76 OR L77 OR L78 OR L79 OR L80
OR L81 OR L82 OR L83)

FILE 'REGISTRY' ENTERED AT 15:32:42 ON 01 FEB 2008

FILE 'CAPLUS' ENTERED AT 15:32:45 ON 01 FEB 2008
D STAT QUE L40
D STAT QUE L41

10/586490

D STAT QUE L42
D STAT QUE L61
D STAT QUE L63
D STAT QUE L66
D STAT QUE L84
L86 34 SEA ABB=ON PLU=ON L40 OR L41 OR L42 OR L61 OR L63 OR L66 OR
L84

FILE 'CASREACT' ENTERED AT 15:33:41 ON 01 FEB 2008
D STAT QUE L72

FILE 'USPATFULL' ENTERED AT 15:34:03 ON 01 FEB 2008
D STAT QUE L44
D STAT QUE L45
D STAT QUE L48
D STAT QUE L51
D STAT QUE L57

L87 24 SEA ABB=ON PLU=ON L44 OR L45 OR L48 OR L51 OR L57

FILE 'STNGUIDE' ENTERED AT 15:35:01 ON 01 FEB 2008

FILE 'CAPLUS, CASREACT, USPATFULL' ENTERED AT 15:35:24 ON 01 FEB 2008
L88 60 DUP REM L86 L72 L87 (13 DUPLICATES REMOVED)
ANSWERS '1-34' FROM FILE CAPLUS
ANSWERS '35-37' FROM FILE CASREACT
ANSWERS '38-60' FROM FILE USPATFULL
D IBIB ABS HITIND HITSTR L88 1-34
D IBIB ABS HIT L88 35-37
D IBIB ABS KWIC HIT HITSTR L88 38-60

FILE HOME

FILE ZCAPLUS

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FILE REGISTRY

Property values tagged with IC are from the ZIC/VINITI data file provided by InfoChem.

STRUCTURE FILE UPDATES: 31 JAN 2008 HIGHEST RN 1001228-41-6
DICTIONARY FILE UPDATES: 31 JAN 2008 HIGHEST RN 1001228-41-6

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<http://www.cas.org/support/stngen/stndoc/properties.html>

FILE USPATFULL

FILE COVERS 1971 TO PATENT PUBLICATION DATE: 31 Jan 2008 (20080131/PD)
FILE LAST UPDATED: 31 Jan 2008 (20080131/ED)

HIGHEST GRANTED PATENT NUMBER: US7325253

HIGHEST APPLICATION PUBLICATION NUMBER: US2008028492

CA INDEXING IS CURRENT THROUGH 31 Jan 2008 (20080131/UPCA)

ISSUE CLASS FIELDS (/INCL) CURRENT THROUGH: 31 Jan 2008 (20080131/PD)

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USPTO MANUAL OF CLASSIFICATIONS THESAURUS ISSUE DATE: Dec 2007

FILE CASREACT

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FILE CONTENT:1840 - 26 Jan 2008 VOL 148 ISS 5

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10/586490

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This file contains CAS Registry Numbers for easy and accurate substance identification.

FILE STNGUIDE
FILE CONTAINS CURRENT INFORMATION.
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